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THE NITROGEN ISOTOPIC SEPARATION FACTORS OF VARIOUS ORGANIC
AMINES ON AMBERLITE IR-120 CATION EXCHANGE RESIN

by

Duane Dale Nowlin

A Dissertation Submitted to the
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1964

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INTRODUCTION

In 1937, Taylor and Urey (1) discovered that when an ion-exchange material was added to a solution of lithium chloride, the lithium-6 was preferentially adsorbed over lithium-7. The reaction can be written as:



where Z represents the solid lattice of the ion-exchange material. In order to determine the effectiveness of such a reaction in the material separation of the isotopes, a determination of the separation factor must be made. The separation factor is given by the ratio ${}^6\text{LiZ}:{}^7\text{LiZ}/{}^6\text{Li}^+:{}^7\text{Li}^+ = \alpha$. If α were large enough, a single-stage equilibrium would be adequate for its determination. However, it is small in most isotopic exchange reactions; and, consequently, a multi-stage equilibrium must be used in its determination. By successive equilibrations of fresh ion-exchange material with the lithium chloride solution, Taylor and Urey (2) found the separation factor to be 1.022. Glueckauf, Barker and Kitt (3) reviewed Taylor and Urey's work and concluded that $(\alpha - 1)$ was probably a factor of 10 smaller than the value reported for the batch experiment. Blanco, Sessions, Kibbey and Roberts (4) repeated Taylor and Urey's work but were unable to reproduce their results. For the batch-type experiment using lithium chloride solution and Na^+ -form

Decalso (sodium aluminum silicate exchanger), a separation factor of 1.00 was found. For the reverse process, i.e., Li^+ -form Decalso vs. sodium chloride solution, α was estimated to be 1.0058 ± 0.0098 . In two column experiments, α was found to be 1.0083 in one, and 1.0038 in the other.

In 1955, Powell, Spedding and Svec (5, 6) developed a continuous ion-exchange process for separating nitrogen isotopes. In this continuous method, separation is effected by loading a quantity of ammonium hydroxide onto a column of cation-exchange resin initially in the hydrogen form. The ammonium band is then eluted down the column with a solution of sodium hydroxide. As the ammonium band travels down the column, the leading edge is slowly depleted in nitrogen-15 and the trailing edge is slowly enriched in this isotope. If a very long ion-exchange column is used, the front and rear edges of the developed ammonium band will contain essentially pure nitrogen-14 and nitrogen-15, respectively.

The fact that nitrogen isotopes can be separated by eluting ammonium ions down an ion-exchange column suggests that perhaps even substituted ammonium compounds--amines--can be used in enriching nitrogen isotopes on ion-exchange columns.

The object of the research performed for this dissertation was to determine the nitrogen isotopic separation factors when various organic amines are brought into con-

tact with the cation-exchange resin Amberlite IR-120. It is hoped that such information will lead to a better understanding of isotopic separation factors and to more efficient and economical methods of separating isotopes.

REVIEW OF LITERATURE ON ION-EXCHANGE SEPARATION OF ISOTOPES

Methods of Determining Separation Factors

There are three basic methods used to determine isotopic separation factors on ion-exchange resins--batch equilibrium, elution chromatography and displacement chromatography. All three methods yield excellent results, however, the latter two methods are generally less time consuming and have almost completely replaced the batch equilibrium method.

Batch equilibrium

Batch equilibrium was the first method used to determine separation factors. Taylor and Urey (1, 2) used this method when they measured the lithium isotopic separation factor. To a solution of lithium chloride, they added a small quantity of Decalso. They allowed the mixture to come to equilibrium and then filtered off the Decalso. This process was repeated several times, using fresh Na^+ -form Decalso each time, until the original lithium concentration was reduced by a factor of 70. The separation factor α is then given approximately by the Rayleigh distillation formula,

$$\left[\frac{1 - N_0}{1 - N} \right]^{\frac{1}{\alpha - 1}} \left[\frac{N}{N_0} \right]^{\frac{\alpha}{\alpha - 1}} = \frac{W_0}{W} \quad (1)$$

where N_0 is the mole fraction of lithium-7 in the initial amount of material W_0 , and N is the mole fraction in the final amount of material W . This method has the disadvantage of being time consuming and laborious.

In addition to Equation 1, Roberts (7) lists several equations that are useful, when using the batch equilibrium method, in calculating separation factors.

Elution chromatography

In addition to batch experiments, Taylor and Urey (1, 2) tried to separate lithium isotopes by utilizing a chromatographic technique. They eluted lithium ions down a column of Na^+ -form zeolite with a dilute sodium chloride solution. They reported a significant isotope enrichment, but lack of an adequate method for the calculation of α from fixed-bed column data prevented a complete evaluation of the method.

In 1941, Martin and Synge (8) recognized the similarity between the chromatographic elution technique and the process occurring in distillation columns. They developed a theory, which was later expanded by Mayer and Thompkins (9), that enabled separation factors to be calculated from elution chromatography data. The assumptions made in their calculations were based on a model that pictured the ion-exchange column as a discontinuous, step-wise process simi-

lar to a distillation column. This is an over simplification of the elution chromatography process and is not accurate enough for calculating separation factors.

Jury (10) was the first to develop a differential equation that adequately explained the isotopic separation process occurring in elution chromatography. He applied his technique to the work done by Gross (11) on the separation of lithium isotopes and obtained an α of 1.0065. Jury's work was refined by Glueckauf, Barker and Kitt (3) and later simplified by Glueckauf (12). According to Glueckauf's development, the concentration of each isotope may be represented approximately by,

$$c_1 = \frac{m_1}{v_1^*} \sqrt{\frac{N}{2\pi}} \exp \left[- \frac{N}{2} \frac{(v_1^* - v)^2}{vv_1^*} \right] \quad (2)$$

where

c_1 = concentration of isotope 1 in effluent,

m_1 = number of milliequivalents of isotope 1 loaded on the column,

v_1^* = volume of effluent at which the maximum concentration c_1^* is noted,

v = volume of effluent solution,

N = number of theoretical plates in the column (obtained from shape of experimentally determined elution curve).

The separation factor α is given by the ratio of the two peak elution volumes.

$$\alpha = 1 + \xi = \frac{v_2^*}{v_1^*} \quad (3)$$

Equation 2 can now be transformed into

$$\ln \left[\frac{c_1}{c_2} / \frac{m_1}{m_2} \right] = \ln \left[\frac{c_1}{c_2} / \frac{c_1^0}{c_2^0} \right] = N\xi \frac{v^* - v}{\sqrt{vv^*}} \quad (4)$$

where v^* is the center of the joint elution peak.

Utilizing Equation 4, the separation factor can be obtained in two ways. First, a plot of $\ln \left[\frac{c_1}{c_2} / \frac{c_1^0}{c_2^0} \right]$ against $\frac{v^* - v}{\sqrt{vv^*}}$ gives a line with a slope of $N\xi$.

Secondly, if the isotopic ratios are determined as functions of the total mixture ($\Delta m/m$), then a plot of $\ln \left[\frac{c_1}{c_2} / \frac{c_1^0}{c_2^0} \right]$ against ($\Delta m/m$) on probability graph paper gives a gradient of ξN .

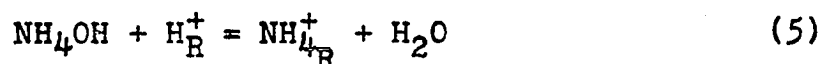
Although the batch equilibrium method uses fewer assumptions when calculating α , the elution chromatography method gives more accurate results, because the total isotopic separations are greater.

Displacement chromatography

In 1955, Powell, Spedding and Svec (5, 6) utilized displacement chromatography to separate large quantities of nitrogen isotopes. They also developed an equation that could be used to calculate separation factors from displacement chromatography data. This method is quite similar to elution chromatography--with one exception. In elution chromatography, the eluting ion and the ion to be eluted have approximately the same affinity for the exchanger. As elution proceeds, there is a continual competition for exchanger sites between the two ions. This causes the elution band to spread out as it travels down the column. An elution band that is a few centimeters in length at the top of an exchange column may be 10 or 20 times that long when it reaches the bottom of the column.

In displacement chromatography, conditions are adjusted so that the displacing ions have a much greater affinity for the exchanger than the retaining ions. This results in a self-sharpening boundary as the displacing solution travels down the column. For example, in separating nitrogen isotopes, a suitable combination would be to have the exchanger in the hydrogen form and to feed ammonium hydroxide as the displacing solution. The H^+ ion is completely displaced by NH_4^+ ion due to the large constant for the reaction which takes place at the front of the band. We can write this re-

action as:



where the subscript R refers to the exchanger phase. When all of the H^+ ions on the exchanger have been replaced by NH_4^+ ions, NH_4OH solution will begin to flow from the column. In the first samples that are collected, the ratio of ^{15}N to ^{14}N , R will be less than the ratio R₀, which existed in the feed. The ratio R will approach R₀ as more effluent solution is collected. When the ratio of ^{15}N to ^{14}N in the effluent becomes equal to the ratio in the feed solution, the separation factor can be calculated by using the following equation,

$$\epsilon = \alpha - 1 = \sum_{i=1}^m \frac{C_1 V_1 (R_0 - R_1)}{QR_0} \quad (6)$$

where V₁ is the volume of the ammonium hydroxide solution collected in the ith fraction and C₁ is its concentration. Q is equal to the number of milliequivalents of resin through which the band moves. This equation will be derived later and a more detailed discussion will be given at that time.

Observed Separation Factors

Separation factors have been determined for a number of elements in the periodic table. The lighter elements have

received the most attention, because the mass difference between two isotopes of a light element is usually very large when compared to the relative mass difference between any two isotopes of a heavier element. For this reason, one would expect to observe larger separation factors for the lighter elements.

Lithium

The separation factor for lithium isotopes has been widely investigated by a number of workers. The interest in this element stems from the fact that it is the lightest of the metallic elements, and it was the first element to be isotopically separated by ion exchange. The controversy over the originally reported lithium separation factor has also created considerable interest in this element.

Taylor and Urey (1, 2) were the first to study isotope separation by ion exchange. Using a sodium aluminum silicate exchanger (Decalso), a LiCl solution and a batch technique, Taylor and Urey determined the lithium isotopic separation factor to be 1.022. Glueckauf, Barker and Kitt (3) used elution chromatography on a column of sulfonated coal-type exchanger to study the separation factor. They concluded the value should be 1.002. Gross (11) also used an elution chromatography technique. He used a column of Dowex-50 resin and eluted the Li^+ band with dilute HCl. He

observed a significant separation of the lithium isotopes, but lack of an adequate method for calculating α prevented evaluation of the system. Jury (10) was the first to develop an equation for calculating separation factors from column elution data. Using the data obtained by Gross, Jury calculated the lithium factor to be 1.0065.

Higgins and Roberts (13, 14, 15, 16) developed a continuous countercurrent ion-exchange unit suitable for commercial separation of isotopes. With this equipment, they measured an α of 1.0029 for the lithium acetate-Dowex-50 resin system. Although their experiment gave greater isotopic fractionation than the batch method, error was introduced into the final answer because α was calculated from an HTU (height of a theoretical unit) value which was only approximate. Another system for separating macro amounts of lithium isotopes was developed by Bresler and Egorov (17). They achieved fractionation of lithium isotopes by adsorbing lithium acetate on a column of H^+ -form SBS-1 resin and eluting with Ca^{++} . A patent issued to J. G. Dean (18) describes a process for separating the isotopes of both potassium and lithium with an inorganic zeolite. However, no separation factors were calculated.

Blanco, Sessions, Kibbey and Roberts (4) repeated Taylor and Urey's original work. They used the same type of exchanger (Decalso), a $LiCl$ solution and the batch equi-

librium technique. For the experiment in which LiCl solution was batch extracted by successive equilibrations with Na⁺-form Decalso, they failed to show any significant fractionation of the lithium isotopes. In a second experiment, Li⁺-form Decalso was batch extracted by successive equilibrations with NaCl solution. In this case, α was found to be 1.0058 ± 0.0098 . In a similar experiment, Lindner and Bergdahl (19) reported $\alpha = 1.0049$ when Li⁺-charged Ionac C-100 zeolite was successively treated with NaCl solution. Blanco *et al.* (4) also ran two column experiments similar to those run by Taylor and Urey. They eluted a Li⁺ band down a column of Na⁺-form Decalso with a NaCl solution and obtained values for α of 1.0083 and 1.0038. Due to certain assumptions that were made in calculating the latter value, they concluded that 1.0083 was probably more accurate.

In another experiment, Blanco, Kibbey, Land and Roberts (20) repeated Taylor and Urey's work, but they used a 12 percent crosslinked Dowex-50 resin instead of an inorganic exchanger. After 15 successive batch equilibrations with LiCl solution, they measured an α of 1.0027 with a 95 percent confidence level of 1.0015 to 1.0050. Perret, Rozand and Saito (21) found a separation factor of 1.002, using a similar batch equilibrium method with Dowex-50 resin and LiNO₃ solution. Studier, Brody and Mech (22), from their column elution experiment, obtained an α of 1.0025 with

H⁺-form Dowex 50 and eluting the Li⁺ with HCl. Also using Dowex 50 and an elution technique, Menes, Saito and Roth (23) reported an α of 1.002. When an inorganic exchanger was used, they found the separation factor increased to 1.004. The value of 1.0027 was confirmed by Lee and Begun (24) for 12 percent crosslinked Dowex-50 resin. With 24 percent crosslinked Dowex 50, they found $\alpha = 1.0038$. With the same type of resin but using displacement chromatography instead of elution chromatography, Powell (25) reported $\alpha = 1.0026 \pm 0.0003$.

The lithium isotopic separation factors that are reported above have been determined by a number of independent workers. To measure these selectivity coefficients, they have used a variety of methods, lithium solutions, concentrations, temperatures and ion exchangers--both organic and inorganic; natural and synthetic. All of these variables can, and probably do, have an affect upon α . Several of the more recent papers have made an attempt to investigate what affect some of the above variables have on changing the separation factor.

Lee (26) determined that the lithium separation factor decreased with an increase in temperature. He found that α varied from 1.0033 at 3°C. to 1.0026 at 59°C. By plotting $\log \alpha$ vs. $1/T$, Lee was able to obtain the heat of exchange ($\Delta H^0 = -2.26$ cal./mole) and entropy change ($\Delta S^0 = -1.81 \times 10^{-3}$

cal./mole degree) at 25°C. Lee (27) also found that the nature of the solution phase affected the separation factor. He concluded that any ions--cation or anion--that tend to destroy the strong $\text{Li}^+(\text{H}_2\text{O})_x$ hydration complex will increase the separation factor. Kakihana, Nomura and Mori (28) supported this theory when they showed that the addition of acetone or ethanol to the lithium solution caused an increase in the separation factor. They were able to achieve a selectivity coefficient as high as 1.022 by using a highly crosslinked resin and 0.1M LiOH in 20 percent acetone-water solution.

Lee (29) reported that the separation factor was influenced by the functional groups on the exchanger. He observed that by using a wide variety of organic and inorganic exchangers, the separation factor varied significantly even under the same conditions. Panchenkov (30) found that the functional groups on the exchanger are influenced by the ionic concentration of the external solution, and the separation factor, in turn, is affected by the functional groups. As the concentration increases, the separation factor increases. The exchanger used in this study was a sulfocoal exchanger with -OH, -COOH and $-\text{SO}_3\text{H}$ active groups on it. These groups become active at different pH's (LiOH concentrations) and, thereby, affect the value of α . Lee (27) also reported that the hydroxyl concentration influ-

ences the separation factor. His explanation was that the hydroxyl ion is a strong proton acceptor which can disrupt the water dipoles around the lithium ion by bonding to protons of the hydration water, effectively causing dehydration.

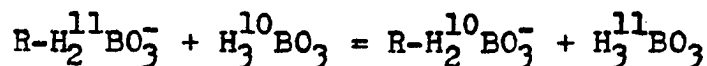
Knyazev and Sklenskaya (31) investigated the effect of chelating agents on the separation factor. They studied the isotopic exchange equilibria between the aquo complex of lithium and its chelates with NTA, EDTA and aminobarbituric-N,N-diacetic acid in aqueous solution. The separation factors are 1.018 ± 0.002 , 1.027 ± 0.001 and 1.076 ± 0.004 , respectively. They explained this trend by assuming differences in bond strengths of Li^+ with the functional groups of the chelate. The EDTA value conflicts with that found by Lee (27) who reported that EDTA lowered the separation factor to 0.998. Blanco and Roberts (32) reported that the complexing agent EDTA had no effect upon the lithium separation factor. In another paper, Knyazev (33) reported that selectivity coefficients obtained with the 10 percent crosslinked resin KU-2 agreed well with those values obtained for similar resins such as Dowex 50 and Amberlite IR-120.

Ciric and Pupezin (34, 35) determined lithium α 's for LiCl , LiNO_3 , Li_2SO_4 , LiOAc and LiOH solutions on Amberlite

IR-120. For the sulfate, acetate and hydroxide compounds, the separation factor was about the same and did not vary significantly with concentration. For the chloride and nitrate solutions, the separation factor increased initially and then decreased as the concentration was increased. They concluded that ion associations in the chloride and nitrate solutions caused the observed variation in α .

Boron

The boron isotopic separation factor has been determined by Yoneda, Uchijima and Makishima (36). They reported that the lighter isotope ^{10}B is enriched in the resin phase. The separation factor for the exchange reaction



was calculated according to Equation 6. Preliminary experiments have shown that the separation factor increases with decreasing boric acid concentrations. The presence of glycerol, which is known to increase the acidity of boric acid solutions, also tends to increase the fractionation factor. For aqueous 0.03M H_3BO_3 , α was calculated as 1.010 and with 0.1M H_3BO_3 in 8 percent glycerol-water solution $\alpha = 1.016$. Glycerol evidently causes a greater ionization of boric acid which accounts for the change in the value of α .

Carbon

Davidson, Mann and Sheline (37, 38) were the first to separate carbon isotopes by ion exchange. They achieved fractionation of the carbon isotopes by using displacement chromatography with an acetate-formic acid-hydrochloric acid system on strongly basic Dowex-2 resin. Experiments utilizing ^{14}C -labeled formic acid solutions indicated the lighter ^{12}C to be enriched in the resin phase. As expected, the separation factor was found to increase with decreasing temperature from 1.0032 at 35.4°C . to 1.0062 at 6.0°C . They also determined α as a function of the percentage of cross-linking in the resin. It varied from 1.0028 for resin with 2 percent DVB (divinylbenzene) content to 1.0059 for 10 percent DVB resin. From the temperature dependence of α , ΔH° for the equilibrium



was calculated to be -4.3 cal./mole, and ΔS° was found to be -6.3×10^{-3} cal./mole-degree at 25°C .

Davidson (39) attempted to investigate the OH^- -- HCN -- HCl system on Dowex-2 resin, but because of resin decomposition, α could not be determined. However, $(\alpha - 1)$ was estimated to be at least six times as great as that for the formic acid system.

Nitrogen

With the exception of lithium, nitrogen has probably received more attention than any other of the light elements in the periodic table. This interest arises from the remarkable separation of nitrogen isotopes achieved by Powell, Spedding and Svec (5, 6). By eluting NH_4OH down a series of connected ion-exchange columns, they were able to obtain 99 percent pure ^{15}N from a starting material containing only 0.365 percent ^{15}N . The separation factor for nitrogen was determined by Powell *et al.* as 1.0257 and confirmed by Comas *et al.* (40). The latter group of workers also investigated the ammonium acetate and ammonium chloride systems. They found that NH_4OH gave a higher separation factor than the other two ammonium compounds. In another paper, Spedding (41) elaborates on the equipment and techniques used to separate macro amounts of isotopes on ion-exchange columns.

Using 0.1M NH_4Cl solution and Dowex-50 resin, Kakihana, Nomura and Kodaira (42) investigated the effect of ethanol upon the nitrogen separation factor. They found α varied from 0.999 to 1.006 with the maximum value occurring at 20-30 volume percent ethanol. They also found an appreciable increase in α with increased crosslinking of the resin. The same group of workers (43) also studied the effect of acetone upon the separation factor. This time they used an

NH_4OH solution, and they found α ranged from 1.023 to 1.034. The highest value was obtained with 55 percent crosslinked exchanger and 40 volume percent acetone.

Oxygen

There have not been any direct ion-exchange studies made of the oxygen isotopic separation factor. However, in a note to the editor, Holmberg (44) discusses an experiment in which sulfur isotopes were fractionated on a Dowex 2-X10 anion-exchange column. In this experiment, an aqueous solution of SO_2 was adsorbed on a column of acetate-form Dowex 2-X10 and displaced with chloride ion. Not only was a fractionation of the sulfur isotopes noted, but the carbon and oxygen isotopes in the effluent acetate also separated to a small extent. The carbon selectivity coefficient was estimated to be 1.0016 (the ^{13}C concentrated in the solution phase) and the oxygen α was estimated as 1.0036 (the ^{18}O concentrated in the solution phase).

Sodium

Edinoff (45) suggested a procedure, using radioisotopes, to measure the separation factors of several elements, including sodium. Harris, Betts and Stevenson (46) used a variation of Edinoff's suggested procedure when they investigated the fractionation of ^{22}Na - ^{24}Na on Dowex 50. They reported that the lighter nuclide was preferentially

held on the resin, but no separation factor was calculated. At 48°C. and 68°C., Harris et al. found that no fractionation occurred on the column. Glueckauf (47) used the data of Harris et al. and calculated sodium α 's of 1.000178, 1.000138 and 1.00007 at 5°, 25° and 55°C., respectively. From this temperature dependence of α , the heat of exchange ($\Delta H^\circ = -0.41$ cal./mole) and entropy change ($\Delta S^\circ = -1.1 \times 10^{-3}$ cal./mole-degree) were calculated.

Kakihana et al. (48, 49) investigated the ^{23}Na - ^{24}Na exchange on Dowex-50 resin using various ethanol-water mixtures. They also studied the effect of resin crosslinking and concentration upon the separation factor. They concluded that the selectivity coefficient was more dependent upon the dielectric constant of the solvent and the concentration of the sodium chloride in the external solution than on the crosslinkage of the resin. The separation factors varied from 0.889 to 1.071. An equation was derived that related the separation factors to the dielectric constant of the external liquid solvent.

Sulfur

Forberg et al. (50) investigated the separation of sulfur isotopes on Dowex-2 anion resin. They eluted NH_4HSO_3 down the column with HCl and reported $\alpha = 1.0100 \pm 0.0005$. Holmberg (44) noted the selectivity coefficient for the

elution of aqueous SO_2 down a column of Dowex 2 as 1.0064. The resin was initially in the acetate form. Powell and Spedding (51) also determined the sulfur separation factor, but they used a different system. They passed an aqueous solution of H_2S down a column of OH^- -form Permutit-SK anion-exchange resin. They found that the resin preferentially adsorbed sulfur isotopes in the following order, $^{34}\text{S} > ^{33}\text{S} > ^{32}\text{S}$. Powell and Spedding measured $\alpha_{32}^{34} = 1.012$ and $\alpha_{33}^{34} = 1.0061$. From these two values, they calculated $\alpha_{33}^{34} = 1.006$ from the relationship $\alpha_{32}^{34} = \alpha_{33}^{34} \cdot \alpha_{32}^{33}$.

Chlorine

Langvad (52) found a fractionation of chlorine isotopes when he eluted KCl down an anion-exchange column of Amberlite IRA-400 with KNO_3 . The ^{35}Cl was preferentially held on the resin over ^{37}Cl . No separation factor was calculated for the reaction.

Potassium

The first potassium isotope fractionation by ion exchange was performed by Taylor and Urey (2). Their column experiments indicated that the heavier ^{41}K isotope was adsorbed more strongly on the resin, and the ^{39}K tended to concentrate in the solution phase. They made no attempt to calculate a separation factor. The only other reference to

the ion-exchange fractionation of potassium isotopes is in a paper by Glueckauf (53). He attempted to calculate the potassium selectivity coefficient from the known radii of the isotopes. He theorized that there is a close analogy between ion-exchange resins and concentrated aqueous solutions. Glueckauf calculated a theoretical potassium separation factor from the activity coefficients of concentrated and dilute aqueous solutions. For ^{39}K - ^{40}K , he predicted $\alpha = 1.000018$. At the present time, the literature contains no experimental evidence to support or deny this theoretical value.

Calcium

Lindner (54) observed that calcium-45 concentrated on Dowex-50 resin in preference to calcium-40, however, no selectivity coefficient was reported.

Titanium

The fractionation of titanium isotopes was discovered quite by accident. In an attempt to separate a mixture of titanium, zirconium and thorium by ion exchange, Brown and Rieman (55) observed that radioactive ^{51}Ti concentrated at the rear of the titanium band when being eluted with citric acid. No α was calculated.

Iron

Knyazev and Mikhailichenko (56) reported that the heavier ^{59}Fe isotope concentrated in the tail fraction of an iron band being eluted with citric acid on a cation-exchange column.

Uranium

Sandstone formations in Western United States have provided a natural exchange media for uranium isotope fractionation. Roshost, Shields and Garner (57) found differences in the ^{235}U to ^{234}U ratios ranging from 40 percent excess ^{234}U to 40 percent deficient ^{234}U . They found that ^{234}U was leached preferentially from the sandstone.

Kakihana et al. (58) eluted U^{+4} and U^{+6} on an anion column with 8N HCl. They found that uranous ions gave a better separation factor ($\alpha = 0.9993$) than uranyl ions ($\alpha = 1.0000$). A mixed solution of uranous and uranyl ions gave a very good separation factor which they explained by the isotope effect in the electron exchange reaction



Table 1 contains a list of those elements whose isotopes have been separated by ion exchange. It is natural to expect that the difference in mass between isotopes governs, to some extent, the selectivity coefficient in the

Table 1. List of isotopes fractionated by ion exchange

Isotopes investigated	Resin preference	Reference
$^6\text{Li} - ^7\text{Li}$	^6Li	1, 2, 3 <u>et al.</u>
$^{10}\text{B} - ^{11}\text{B}$	^{10}B	36
$^{12}\text{C} - ^{14}\text{C}$	^{12}C	37, 38, 39
$^{14}\text{N} - ^{15}\text{N}$	^{15}N	5, 6, 40
$^{16}\text{O} - ^{18}\text{O}$	^{16}O	44
$^{22}\text{Na} - ^{24}\text{Na}$	^{22}Na	45, 46
$^{23}\text{Na} - ^{24}\text{Na}$	$^{24}\text{Na}^*$	48, 49
$^{32}\text{S} - ^{34}\text{S}$	^{34}S	44, 50, 51
$^{32}\text{S} - ^{33}\text{S}$	^{33}S	51
$^{35}\text{Cl} - ^{37}\text{Cl}$	^{35}Cl	52
$^{39}\text{K} - ^{41}\text{K}$	^{41}K	2, 53
$^{40}\text{Ca} - ^{45}\text{Ca}$	^{45}Ca	54
$^{48}\text{Ti} - ^{51}\text{Ti}$	^{51}Ti	55
$^{56}\text{Fe} - ^{59}\text{Fe}$	^{59}Fe	56
$^{234}\text{U} - ^{235}\text{U}$	^{235}U	57
$^{235}\text{U} - ^{238}\text{U}$	^{235}U	58

*In aqueous solution, the ^{24}Na was preferentially adsorbed on the resin, but in ethanol-water solutions ^{23}Na was more strongly retained on the resin.

ion-exchange equilibrium. However, the relationship between the selectivity coefficient and the mass number of an isotope is not a simple one, as can be seen from the previous table.

Theoretical Determination of Separation Factors

A number of statistical equations have been developed (59, 60, 61, 62, 63) that explain the direction and degree of isotopic enrichment in certain gas-gas and gas-liquid exchange reactions. However, these expressions are rigorous only when there is no interaction between molecules. Also, the molecules must be considered as rotating rigidly and vibrating harmonically with no rotational-vibrational interaction. In condensed media involving ion exchangers, intermolecular forces cannot be ignored and statistical equations explaining isotopic fractionation are much more complicated. At the present time, no completely satisfactory equation has been developed to explain the ion-exchange separation factor.

The previous section was devoted primarily to papers involved with experimentally determined separation factors for various elements. These papers are by far the most numerous. This section of the thesis will review those papers that emphasize the theoretical aspect of α and seek to explain some of the anomalies that exist in the literature.

According to Kakihana et al. (64, 65, 66, 67), the separation factor is directly influenced by the type of ion associations occurring in the solution phase as compared to those occurring in the resin phase. If the ion of interest is in very nearly the same state, both in the solution and in the exchanger, then the isotopic selectivity coefficient will be very small. On the other hand, if the chemical binding is very different in the two phases, the separation factor will be relatively large. This is the same conclusion reached by Glueckauf and Kitt (68). Starting with the basic principles involved in the ion-exchange separation of isotopes, Kakihana et al. derived an equation that can be used to calculate α . By making certain assumptions and approximations, this equation can be greatly simplified to quantitatively predict separation factors. From the nature of the equation, these workers predicted that larger separation factors might be obtained from:

- (1) A system containing molecules or ion associations in either the exchanger or solution phase may give a larger α than a system containing only strong electrolytes in both phases. The larger the amounts of molecules or ion associations, the larger the separation factor.

- (2) A system containing molecules or ion associations in both phases may not give a larger α due to cancelling of terms in the equation. However, if an exchanger has the ability to form a different type of chemical binding with the isotopes from that in the external solution, the cancellation can be avoided.

Bresler (69) has developed a differential equation that describes the isotope separation process in a chromatographic column. The solution of the equation gives the maximum separation and the time required to reach the steady state distribution. The formulas obtained were satisfactorily applied to the data of Powell *et al.* (5, 6) on the separation of nitrogen isotopes.

Knyazev (70) calculated separation factors for Li, Na, K, Rb, Cs, Mg, Ca, Sr, Cl, Br and I that agree well with those experimental values reported in the literature. From his calculations, Knyazev concluded that the best separation should occur with multivalent ions of small mass.

Davies and Owen (71) investigated the behavior of ion-exchange resins in mixed solvents. They found that the resin phase was predominantly aqueous, and the external solution phase was predominantly organic. The opportunity now arises of using partition effects to enhance the normal

separation factor. This is perhaps the explanation for the higher separation factors reported by several of the workers using ethanol-water and acetone-water systems.

Freeman (72) discovered that the distribution of strong electrolyte between an aqueous solution and an ion-exchange resin was regular at moderate concentrations, but at low concentrations, uncommonly large amounts of electrolyte appear to enter the exchanger phase. This may explain the concentration dependence of α that was reported earlier.

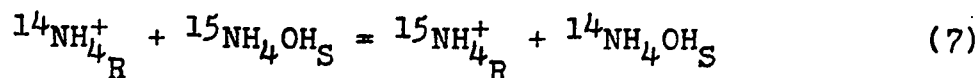
Two reviews on isotope separation have appeared recently in the literature. The first, by Chemla (73), discusses 45 references pertaining to the separation of isotopes by chromatography and by electrophoresis. The second review, containing 22 references, is by Glueckauf (74). He compares the separation of isotopes by gas and ion-exchange chromatography.

MATHEMATICAL COMPUTATION OF SEPARATION FACTORS

The equation used in this work for the calculation of separation factors is the same as that developed by Powell, Spedding and Svec (6). Much of the following derivation has been taken from their paper.

If one passes a dilute aqueous solution of organic amine down a bed of cation exchanger in the H^+ cycle, the H^+ ion is completely displaced by the organic-ammonium radical, due to the large equilibrium constant for the reaction which takes place at the front of the band. For the simplest of the amines--ammonia--the reaction is given by Equation 5. The reaction is the same for the higher amines, however, one or more of the hydrogens on the ammonium ion is replaced by an organic radical.

When all of the H^+ ion on the resin has been replaced by NH_4^+ ion, NH_4OH solution begins to flow from the resin bed. In the first few fractions that are collected, the ratio of ^{15}N to ^{14}N , \underline{R} , will be less than the ratio \underline{R}_0 which existed in the feed solution, due to the isotopic exchange reaction



The subscripts \underline{R} and \underline{S} refer to the resin and solution phases, respectively. As more effluent solution is col-

lected, the ratio \underline{R} approaches \underline{R}_0 . Finally, the ratio in the effluent solution becomes equal to \underline{R}_0 . When this occurs, the ratio of ^{15}N to ^{14}N in the resin phase must differ from \underline{R}_0 by the factor \underline{K} , due to the equilibrium relationship

$$\underline{K} = \frac{(^{15}\text{NH}_4^+)_R (^{14}\text{NH}_4\text{OH}_S)}{(^{14}\text{NH}_4^+)_R (^{15}\text{NH}_4\text{OH}_S)} = \frac{(^{15}\text{N}_R) (^{14}\text{N}_S)}{(^{14}\text{N}_R) (^{15}\text{N}_S)} = \frac{\underline{R}_R}{\underline{R}_S} = \frac{\underline{R}_R}{\underline{R}_0} \quad (8)$$

Now Equation 8 can be written in the form

$$\underline{K} = \frac{\underline{N}_R}{1 - \underline{N}_R} \times \frac{1 - \underline{N}_0}{\underline{N}_0} \quad (9)$$

where \underline{N}_R and \underline{N}_0 are the mole fractions of ^{15}N in the resin bed and feed solution, respectively. \underline{N}_R can be written

$$\underline{N}_R = \frac{\underline{n}}{\underline{Q}} \quad (10)$$

where \underline{Q} is the total exchange capacity of the resin bed in equivalents and \underline{n} is the total number of equivalents of $^{15}\text{NH}_4^+$ adsorbed on the resin.

If \underline{K} in Equation 8 turned out to be exactly 1, then there would be no tendency for either enrichment or depletion of $^{15}\text{NH}_4^+$ in the resin phase when it is equilibrated with a solution of ammonia. That is, $\underline{n}_0/\underline{Q}$ would equal \underline{N}_0 . However, if \underline{K} differs from 1, then \underline{n} can be defined as

$$\underline{n} = \underline{n}_0 + \Delta \underline{n} \quad (11)$$

Equation 10 now becomes

$$N_R = \frac{n_o + \Delta n}{Q} = N_o + \frac{\Delta n}{Q} \quad (12)$$

Substituting Equation 12 into Equation 9, gives

$$K = \frac{(N_o + \Delta n/Q) (1 - N_o)}{(1 - N_o - \Delta n/Q) N_o} \quad (13)$$

$$= 1 + \frac{\Delta n}{N_o Q (1 - N_o - \Delta n/Q)} \quad (13')$$

and

$$\mathcal{E} = K - 1 = \frac{\Delta n}{N_o Q (1 - N_o - \Delta n/Q)} \quad (14)$$

Solving Equation 14 for $\Delta n/Q$, one obtains the relationship

$$\frac{\Delta n}{Q} = \frac{\mathcal{E} N_o (1 - N_o)}{1 + \mathcal{E} N_o} \quad (15)$$

If \mathcal{E} is small compared to 1, then $\Delta n/Q$ is of the order of $\mathcal{E} N_o (1 - N_o)$ and is also much less than either 1 or N_o .

Consequently, Equation 14 can be written

$$\mathcal{E} = \frac{\Delta n}{Q N_o (1 - N_o)} \quad (16)$$

Now

$$\Delta n = \Delta n_{\text{resin}} = -\Delta n_{\text{effluent}} \quad (17)$$

so

$$\Delta n = \sum_{i=1}^m V_i C_i (N_o - N_i) \quad (18)$$

where

V_i = volume of the i th fraction,

C_i = concentration of ammonia in the i th fraction,

N_i = mole fraction of ^{15}N in ammonia of the i th fraction of the m fractions that were collected,

N_o = mole fraction of ^{15}N in ammonia of the feed solution.

Equation 18 now becomes

$$\varepsilon = \frac{\sum_{i=1}^m V_i C_i (N_o - N_i)}{Q N_o (1 - N_o)} \quad (19)$$

The mole fraction of ^{15}N can be written

$$N_i = \frac{R_i}{1 + R_i} \quad (20)$$

and

$$N_o = \frac{R_o}{1 + R_o} \quad (21)$$

Substituting Equations 20 and 21 into Equation 19 and cancelling terms, gives

$$\xi = \frac{\sum_{i=1}^m V_i C_i \left[\frac{R_0}{1 + R_0} - \frac{R_1}{1 + R_1} \right]}{\frac{QR_0}{(1 + R_0)^2}} \quad (22)$$

Finally, since \underline{R}_0 for normal nitrogen is $0.00365(1 + \underline{R}_1) \cong (1 + \underline{R}_0) \cong 1.00$ and

$$\xi = \alpha - 1 = \sum_{i=1}^m \frac{C_i V_i (R_0 - R_1)}{QR_0} \quad (6)$$

If extremely high precision is desired and experimental accuracy warrants, $\underline{\xi}$ can be determined from Equation 14 at the expense of more involved computations. In this work, Equation 6 was used for the determination of $\underline{\xi}$.

EXPERIMENTAL DETAILS

Preparation of Reagents

Ammonium hydroxide solution

A quantity of 29.23 grams of 29 percent ammonium hydroxide (J. T. Baker Chemical Company) was diluted to four liters with distilled water. A small portion of this solution was titrated with standard H_2SO_4 , and the concentration was found to be 0.1249N.

Methylamine solution

A quantity of 38.75 grams of 40 percent methylamine (Matheson Coleman & Bell) was diluted to four liters with distilled water. A portion of this solution was titrated against standard H_2SO_4 and gave a concentration of 0.1252N.

Ethylamine solution

A quantity of 23.0 grams of anhydrous ethylamine (Eastman Organic Chemical Company) was diluted to four liters with distilled water. Titrating a portion of this solution against standard H_2SO_4 , the concentration was found to be 0.1305N.

n-Propylamine solution

A bottle of anhydrous n-propylamine (Matheson Coleman & Bell) was found to have a slight yellow color so it was

fractionally distilled prior to use. The first and last portions were discarded and the colorless middle portion was used in this work. A quantity of 30.0 grams of the anhydrous amine was diluted to four liters with distilled water. Titration with standard acid gave a concentration of 0.1251N.

iso-Propylamine solution

A quantity of 29.56 grams of anhydrous iso-propylamine (Matheson Coleman & Bell), fractionally distilled prior to use, was diluted to four liters with distilled water. Titration with standard acid gave a concentration of 0.1240N.

n-Butylamine solution

A quantity of 37.0 grams of anhydrous n-butylamine (Matheson Coleman & Bell), fractionally distilled prior to use, was diluted to four liters with distilled water. Titration with standard acid gave a concentration of 0.1323N.

Dimethylamine solution

A quantity of 23.0 grams of anhydrous dimethylamine (Eastman Organic Chemical Company) was diluted to four liters with distilled water. Titration with standard acid gave a concentration of 0.1268N.

Diethylamine solution

A quantity of 37.0 grams of anhydrous diethylamine (Matheson Coleman & Bell), fractionally distilled prior to use, was diluted to four liters with distilled water. Titrating a portion of this solution against standard acid, the concentration was found to be 0.1237N.

Dipropylamine solution

A quantity of 50.60 grams of anhydrous dipropylamine (Eastman Organic Chemical Company), fractionally distilled prior to use, was diluted to four liters with distilled water. Titration against standard acid gave a concentration of 0.1226N.

Trimethylamine solution

A quantity of 30.0 grams of anhydrous trimethylamine (Eastman Organic Chemical Company), fractionally distilled prior to use, was diluted to four liters with distilled water. Titration with standard acid gave a concentration of 0.1043N.

Triethylamine solution

A quantity of 51.0 grams of anhydrous triethylamine (Eastman Organic Chemical Company), fractionally distilled prior to use, was diluted to four liters with distilled water. Titration with standard acid gave a concentration of

0.1246N.

Standard potassium hydroxide solution

An approximately 0.1N potassium hydroxide solution was prepared by the method of Powell and Hiller (75) and standardized against potassium acid phthalate.

Standard sulfuric acid solution

An approximately 0.5N sulfuric acid solution was prepared from 96 percent H_2SO_4 (J. T. Baker Chemical Company), and standardized against the standard potassium hydroxide solution above.

Apparatus

Glass columns

The two columns used in this work were glass tubes 125 centimeters long by 1.2 centimeters I. D. The bottoms of the columns were permanently fitted with porous glass plates to retain the resin. A stopcock with a needle valve was attached to the bottom of each column so that the flow rate could be adjusted. The top of each column was fitted with a one-hole rubber stopper. A polyethylene tube ran from the top of each column to a four-liter flask located approximately six inches above the column. These flasks contained the feed solutions.

Ion-exchange resin

The ion-exchange material used in this work was 20-40 mesh Amberlite IR-120-H⁺ resin. It was conditioned by boiling with 6M NaOH according to the method of Betts and MacKenzie (76). After the NaOH treatment, the resin was washed free of base and then converted to the H⁺ cycle by washing with 3M HCl. The two glass columns described above were filled to within 22 centimeters of the top with the conditioned resin. Next, the resin in each column was backwashed for several hours with distilled water to remove any resin fines and to classify the bed.

The capacity of each column was determined by passing a ten percent NaCl solution through the resin column and collecting the effluent HCl in a volumetric flask. An aliquot of this effluent solution was titrated with standard KOH, and the capacity of the resin bed was determined to be 234.5 milliequivalents. Fortunately, both resin columns had identical capacities.

After each amine run was completed, the resin column was backwashed with distilled water, regenerated with 3M HCl and then rinsed free of acid with distilled water. Care was taken not to lose any resin during the backwash step.

At the end of the amine studies, the resin capacities were redetermined and measured as 233.5 milliequivalents.

The average value of 234.0 was used in calculating separation factors.

Mass spectrometer

The instrument used in this work to measure the nitrogen isotopic ratio was a Consolidated-Nier isotope ratio mass spectrometer Model 21-201. The machine had a permanent magnet with a 60° sector and a six-inch radius of curvature. Information concerning the operation of this instrument can be found in the Consolidated Engineering Corporation's operation and maintenance manual (77).

Procedure

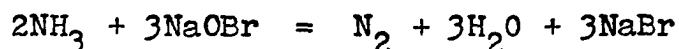
The technique used in this work to determine isotopic separation factors is the same as that used by Powell et al. (6). The eleven amines that were investigated were first checked for purity on a F. and M. Model-500 gas chromatograph. A couple of the amines were slightly yellow in color, and obviously contained small amounts of impurities. These impurities, however, were not detectible on the gas chromatograph. The impure amines and all other amines with boiling points above room temperature were fractionally distilled prior to use.

Approximately one-half mole of the pure amine was diluted to four liters with distilled water. All of the amines were soluble to this extent. Prior to the start of

the separation factor determination, a sample (150 milliliters) of the dilute amine was withdrawn from the four-liter flask and titrated with standard H_2SO_4 . If the concentration varied significantly from 0.125N, it was adjusted at this time. Another sample of the original amine was taken at the end of the separation factor determination. These two amine samples were used to determine the ^{15}N to ^{14}N ratio of the feed solution.

Next, the amine solution was slowly fed into a column of Amberlite IR-120- H^+ resin. The flow rate was not critical, but an attempt was made to keep the flow rate at 1.0 ± 0.5 ml./min. The amine formed a very sharp front boundary as it contacted the resin in the column. This boundary could be watched as it progressed down the column, due to a slightly different color in the two forms of the resin. With the flow rates and solution concentrations used in these experiments, it required approximately 40 hours for the front of the amine band to reach the bottom of the column. When the amine reached within a few centimeters of the bottom, the flow rate was stopped and the column was allowed to remain static overnight. When the flow rate was started again, nine samples (approximately 150 milliliters each) of effluent amine were collected in an excess of standard H_2SO_4 . The milliequivalents of amine in each sam-

ple were determined by back titrating the excess acid with standard KOH, using bromcresol purple indicator. Approximately 30 milliliters of concentrated H_2SO_4 (J. T. Baker Chemical Company), 10 grams of anhydrous Na_2SO_4 (J. T. Baker Chemical Company) and 0.3 grams of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (Hach Chemical Company) were added to each of the amine samples. The samples were then decomposed according to the Kjeldahl method of Diehl and Smith (78). After Kjeldahl decomposition, the samples were made basic with concentrated NaOH solution. The liberated ammonia was collected in an excess of dilute HCl. The acidified ammonia samples were then treated with NaOBr in a special vacuum apparatus to convert the ammonia to free nitrogen. According to Glascock (79), the hypobromite oxidation can be written



Clusius and Rechnitz (80) give a very complete discussion of this reaction. The nitrogen gas liberated from the hypobromite oxidation was collected in sample bulbs and retained for analysis on the Consolidated-Nier mass spectrometer.

The general procedure used to determine the nitrogen isotopic content of the amine samples was as follows. First, a nitrogen sample of known isotopic content ($^{29}\text{N}/^{28}\text{N} = 0.00732$) was admitted into the mass spectrometer, and the

ratio $^{29}\text{N}/^{28}\text{N}$ was measured. The ratio of actual isotopic content to measured isotopic content was used as a correction factor for the amine nitrogen sample. Next, the machine was evacuated and the $^{29}\text{N}/^{28}\text{N}$ ratio was measured again. This value is called the background ratio of the machine, and for this particular instrument it was relatively high. The background ratio must be subtracted from any measurements taken on this machine. Finally, a sample of nitrogen from the amine decomposition was admitted into the mass spectrometer, and its ratio was determined. This value was then corrected for background ratio and standard nitrogen. The corrected values for the amine samples appear in Column 2 of Tables 3-13.

EXPERIMENTAL RESULTS AND DISCUSSION

The nitrogen isotopic separation factors that were determined in this work are listed in Table 2, and the data used to calculate these factors appear in Tables 3-13. A list of the ionization constants of the amines (81) also appears in Table 2. The data in these tables is represented graphically in Figures 1-11. It is generally agreed that there is a gradual increase in the ionization constant in going from ammonium hydroxide to primary amines to secondary amines. This results from the electronic contribution of the alkyl groups to the nitrogen atom. The decrease in the ionization constant of the tertiary amines is due to steric factors. The ionization constants in Table 2 do not follow a smooth trend. This probably results from the fact that they were determined by a number of different workers using various methods and concentrations.

As can be seen from Table 2, there is a gradual decrease in the separation factor as the length of the carbon chain is increased within any single group of amines. This trend may be somewhat fortuitous since the standard error of these values was calculated as ± 0.001 . The decrease in the separation factor that occurs when going from one group of amines to the next, *i. e.*, from primary to secondary to tertiary, is large enough to overshadow the standard error.

Table 2. Nitrogen isotopic separation factors and ionization constants of various organic amines on Amberlite IR-120 resin

Amine	α_{14}^{15}	K
Ammonium hydroxide	1.0254	1.8×10^{-5}
Methylamine	1.0223	5.0×10^{-4}
Ethylamine	1.0218	5.6×10^{-4}
n-Propylamine	1.0199	4.7×10^{-4}
n-Butylamine	1.0183	-----
Dimethylamine	1.0174	5.2×10^{-4}
Diethylamine	1.0172	1.3×10^{-3}
Dipropylamine	1.0159	1.0×10^{-3}
Trimethylamine	1.0130	7.4×10^{-5}
Triethylamine	1.0117	6.4×10^{-4}

Part of the standard error can be attributed to the manner in which the isotopic ratio of the feed solution was chosen. It was mentioned earlier that a sample of the feed solution was titrated at the beginning of the separation factor determination. A second sample was taken at the end of the determination--approximately three days after the initial sample. During the intervening time, the bulk of the feed solution was allowed to stand in a four-liter Erlenmeyer flask covered with a beaker. The solution was

slowly siphoned from this flask into the ion-exchange column. With the exception of one amine (dipropylamine), the sample of feed solution withdrawn at the end of the run always had a higher ^{15}N to ^{14}N ratio than the sample taken at the beginning of the determination. The difference was usually only 0.00002 and the feed solution ratios, as indicated in Tables 3-13, averaged about 0.00365. The reverse effect found with dipropylamine can only be attributed to experimental error.

The changing isotopic concentration of the feed solution can be explained if one assumes that ^{14}N -amine has a higher vapor pressure than ^{15}N -amine. This would mean that the amine of the lighter isotope would evaporate faster and the ^{15}N would concentrate in the solution phase. This is quite logical in view of the evidence found by Urey and Aten (82). They measured the vapor pressure ratio of $^{14}\text{NH}_3/^{15}\text{NH}_3$ and reported a value of 1.0025.

The question now arises as to which ratio--the larger or the smaller--should be taken as the true feed solution value. In most cases, the best curve drawn through the sample data points coincided with the larger feed solution ratio. In the cases of diethyl- and triethylamine (Figures 8 and 11), the data points were quite scattered and an average of the two feed solution ratios gave the best curve.

The differences in the initial and final feed ratios were 0.00007 and 0.00004, for diethyl- and triethylamine, respectively. These differences were greater than observed in any of the other amines and; consequently, an average value was used.

In the past, it has been assumed that small separation factors are a result of similar bonding between the ^{15}N and ^{14}N forms of the amine--both in the resin and solution phases. This explanation is certainly true, but it does very little to quantitatively explain the isotope separation process occurring on ion-exchange resins. A better explanation is given by Kakihana et al. (64, 65, 66, 67). According to these workers, the separation factor is a result of three separate isotopic equilibria. First, in a solution containing isotopic ions A^+ and B^+ at equilibrium with the same ions adsorbed on a cation resin, the reaction can be written



and the equilibrium constant for this reaction is

$$K_w = \frac{(\text{B}_\text{R}^+) (\text{A}^+)}{(\text{A}_\text{R}^+) (\text{B}^+)} \quad (24)$$

If there is a possibility that isotopic ions A^+ and B^+ can

form molecules or ion associations, AX and BX, in the solution phase, then a second isotopic equilibrium exists



and

$$K_x = \frac{(B^+) (AX)}{(A^+) (BX)} \quad (26)$$

The third equilibrium occurs between ions adsorbed on the exchanger, A_R^+ and B_R^+ , and those same ions forming molecules or ion associations, AY and BY, with the exchanger. This reaction is



and

$$K_y = \frac{(B_R^+) (AY)}{(A_R^+) (BY)} \quad (28)$$

Using Equations 23-28, it can be shown that the separation factor α_A^B is given by

$$\ln \alpha_A^B = \ln K_w + \ln K_x - \ln K_y + \ln \left[1 + \frac{K_y - 1}{1 + (AY)/(A_R^+)} \right] - \ln \left[1 + \frac{K_x - 1}{1 + (AX)/(A^+)} \right] \quad (29)$$

In order to use Equation 29 for calculating theoretical separation factors, the concentrations of all ionic and molecular species, both in the resin and solution phases, must be known. Unfortunately, with the present techniques, it is not possible to measure the absolute concentrations of all the ionic and molecular species in the system.

Looking at Equation 29 analytically, Kakihana et al. (65) concluded that, "A system containing molecules or ion associations in the exchanger phase or in the external solution phase may have a chance of giving a larger separation factor than a system containing only strong electrolytes in both phases. In the case mentioned above, the larger the amounts of molecules or ion associations, the larger the separation factor that may be obtained." Since the ionization constant of an amine is a measure of the ions and molecules in the solution phase, we would expect the separation factor to be inversely related to the ionization constant. As the ionization constant increases, the separation factor should decrease. If this were true, then we would expect the separation factor to decrease in going from ammonium hydroxide to primary amines to secondary amines, but increase in going to tertiary amines. Table 2 shows that α continues to decrease with the tertiary amines despite a decrease in the ionization constant. Unless unknown reactions in the resin phase are causing this anom-

Table 3. Experimental mass spectrometer data and calculated values for ammonium hydroxide

Sample	Corrected $\frac{^{29}\text{N}}{^{28}\text{N}}$	$\frac{^{15}\text{N}}{^{14}\text{N}}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00472	0.00236	8.71	0.01316
2	0.00616	0.00308	15.02	0.01002
3	0.00706	0.00353	14.73	0.00207
4	0.00729	0.00364	16.49	0.00019
5	0.00731	0.00365	16.12	0.00000
6	0.00726	0.00363	15.11	0.00000
7	0.00731	0.00365	15.75	0.00000
8	0.00730	0.00365	16.75	0.00000
9	0.00730	0.00365	15.23	0.00000
Feed	0.00730	0.00365	18.11	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $\frac{^{15}\text{N}}{^{14}\text{N}}$ in feed solution = 0.00365

R_1 = $\frac{^{15}\text{N}}{^{14}\text{N}}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 4. Experimental mass spectrometer data and calculated values for methylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00554	0.00277	11.19	0.01183
2	0.00650	0.00325	14.73	0.00736
3	0.00711	0.00355	15.83	0.00239
4	0.00731	0.00365	15.67	0.00055
5	0.00734	0.00367	15.91	0.00018
6	0.00736	0.00368	13.88	0.00000
7	0.00735	0.00367	17.71	0.00000
8	0.00736	0.00368	16.49	0.00000
9	0.00732	0.00366	15.95	0.00000
Feed	0.00736	0.00368	18.60	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00368

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 5. Experimental mass spectrometer data and calculated values for ethylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00583	0.00291	16.52	0.01470
2	0.00676	0.00338	17.01	0.00538
3	0.00718	0.00359	17.92	0.00126
4	0.00726	0.00363	17.48	0.00041
5	0.00732	0.00366	17.15	0.00000
6	0.00728	0.00364	17.62	0.00000
7	0.00731	0.00365	18.88	0.00000
8	0.00731	0.00365	18.36	0.00000
9	0.00731	0.00365	17.65	0.00000
Feed	0.00731	0.00365	19.30	0.00000

^a A_1 = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 6. Experimental mass spectrometer data and calculated values for n-propylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00572	0.00286	7.50	0.00694
2	0.00641	0.00320	16.68	0.00879
3	0.00698	0.00349	14.93	0.00280
4	0.00720	0.00360	16.64	0.00098
5	0.00728	0.00364	16.59	0.00019
6	0.00728	0.00364	14.48	0.00017
7	0.00732	0.00366	15.58	0.00000
8	0.00727	0.00363	16.42	0.00000
9	0.00730	0.00365	18.78	0.00000
Feed	0.00730	0.00365	18.32	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 7. Experimental mass spectrometer data and calculated values for iso-propylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00594	0.00297	14.35	0.01142
2	0.00666	0.00333	15.26	0.00572
3	0.00709	0.00354	17.21	0.00222
4	0.00728	0.00364	16.02	0.00019
5	0.00728	0.00364	16.04	0.00019
6	0.00731	0.00365	15.09	0.00000
7	0.00731	0.00365	15.69	0.00000
8	0.00728	0.00364	17.18	0.00000
9	0.00732	0.00366	16.70	0.00000
Feed	0.00731	0.00365	18.39	0.00000

^a A_1 = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 8. Experimental mass spectrometer data and calculated values for n-butylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00615	0.00307	6.36	0.00426
2	0.00655	0.00327	17.48	0.00759
3	0.00691	0.00345	18.78	0.00419
4	0.00712	0.00356	17.60	0.00165
5	0.00722	0.00361	17.04	0.00060
6	0.00728	0.00364	18.78	0.00000
7	0.00727	0.00363	16.33	0.00000
8	0.00728	0.00364	16.99	0.00000
9	0.00727	0.00363	18.99	0.00000
Feed	0.00728	0.00364	19.85	0.00000

^aA₁ = milliequivalents of amine in ith sample

R₀ = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00364

R₁ = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 9. Experimental mass spectrometer data and calculated values for dimethylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00580	0.00290	12.40	0.01089
2	0.00674	0.00337	17.48	0.00573
3	0.00723	0.00361	17.55	0.00082
4	0.00731	0.00365	17.71	0.00000
5	0.00727	0.00363	17.79	0.00000
6	0.00731	0.00365	17.98	0.00000
7	0.00728	0.00364	17.28	0.00000
8	0.00732	0.00366	16.14	0.00000
9	0.00728	0.00364	18.07	0.00000
Feed	0.00731	0.00365	18.64	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 10. Experimental mass spectrometer data and calculated values for diethylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00617	0.00308	7.24	0.00497
2	0.00649	0.00324	16.19	0.00811
3	0.00703	0.00351	15.69	0.00292
4	0.00723	0.00361	16.49	0.00115
5	0.00735	0.00367	17.22	0.00000
6	0.00731	0.00365	16.24	0.00000
7	0.00727	0.00363	15.96	0.00000
8	0.00736	0.00368	15.82	0.00000
9	0.00751	0.00375	16.89	0.00000
Feed	0.00735	0.00367	18.14	0.00000

aA_1 = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00367

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 11. Experimental mass spectrometer data and calculated values for dipropylamine

Sample	Corrected $\frac{^{29}\text{N}}{^{28}\text{N}}$	$\frac{^{15}\text{N}}{^{14}\text{N}}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00663	0.00331	8.09	0.00339
2	0.00678	0.00339	12.48	0.00407
3	0.00690	0.00345	14.28	0.00366
4	0.00708	0.00354	14.90	0.00226
5	0.00719	0.00359	15.65	0.00146
6	0.00726	0.00363	15.38	0.00072
7	0.00731	0.00365	13.48	0.00031
8	0.00735	0.00367	14.68	0.00000
9	0.00735	0.00367	16.09	0.00000
Feed	0.00735	0.00367	17.79	0.00000

^aA₁ = milliequivalents of amine in ith sample

R₀ = $\frac{^{15}\text{N}}{^{14}\text{N}}$ in feed solution = 0.00367

R₁ = $\frac{^{15}\text{N}}{^{14}\text{N}}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 12. Experimental mass spectrometer data and calculated values for trimethylamine

Sample	Corrected $^{29}\text{N}/^{28}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00624	0.00312	13.12	0.00814
2	0.00687	0.00343	13.49	0.00348
3	0.00714	0.00357	14.71	0.00138
4	0.00731	0.00365	14.08	0.00000
5	0.00732	0.00366	14.12	0.00000
6	0.00731	0.00365	15.70	0.00000
7	0.00724	0.00362	15.42	0.00000
8	0.00743	0.00371	15.42	0.00000
9	0.00731	0.00365	17.41	0.00000
Feed	0.00731	0.00365	12.60	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Table 13. Experimental mass spectrometer data and calculated values for triethylamine

Sample	Corrected 29 28 N/ N	15 14 N/ N	Milli- equiv. amine	$\frac{A_1(R_0 - R_1)^a}{QR_0}$
1	0.00670	0.00335	9.47	0.00333
2	0.00684	0.00342	16.27	0.00438
3	0.00706	0.00353	14.70	0.00207
4	0.00718	0.00359	15.73	0.00111
5	0.00724	0.00362	16.97	0.00060
6	0.00728	0.00364	16.26	0.00019
7	0.00727	0.00363	15.88	0.00000
8	0.00727	0.00363	15.04	0.00000
9	0.00735	0.00367	17.24	0.00000
Feed	0.00731	0.00365	17.02	0.00000

$^a A_1$ = milliequivalents of amine in ith sample

R_0 = $^{15}\text{N}/^{14}\text{N}$ in feed solution = 0.00365

R_1 = $^{15}\text{N}/^{14}\text{N}$ in ith sample

Q = capacity of resin bed in milliequivalents = 234.0

Figure 1. A plot of $\delta^{15}\text{N}$ versus sample number for the ammonium hydroxide system

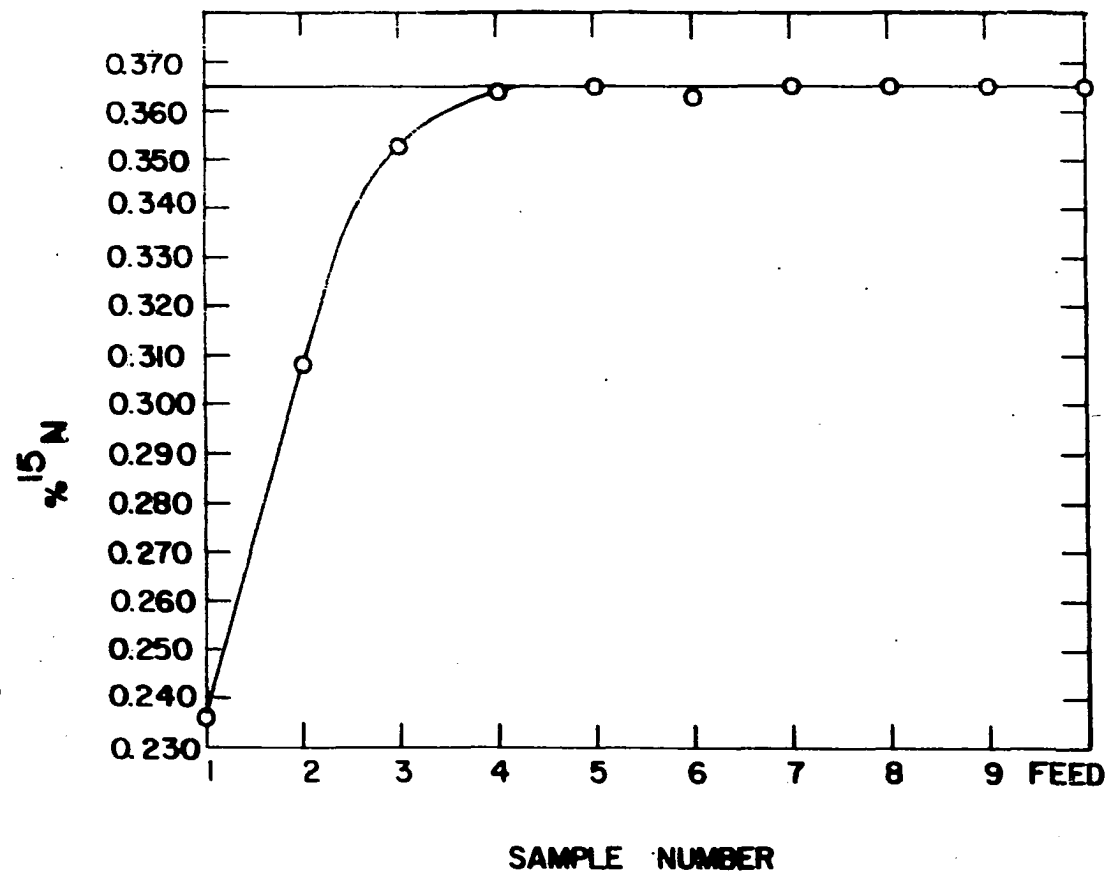


Figure 2. A plot of % ^{15}N versus sample number for the methylamine system

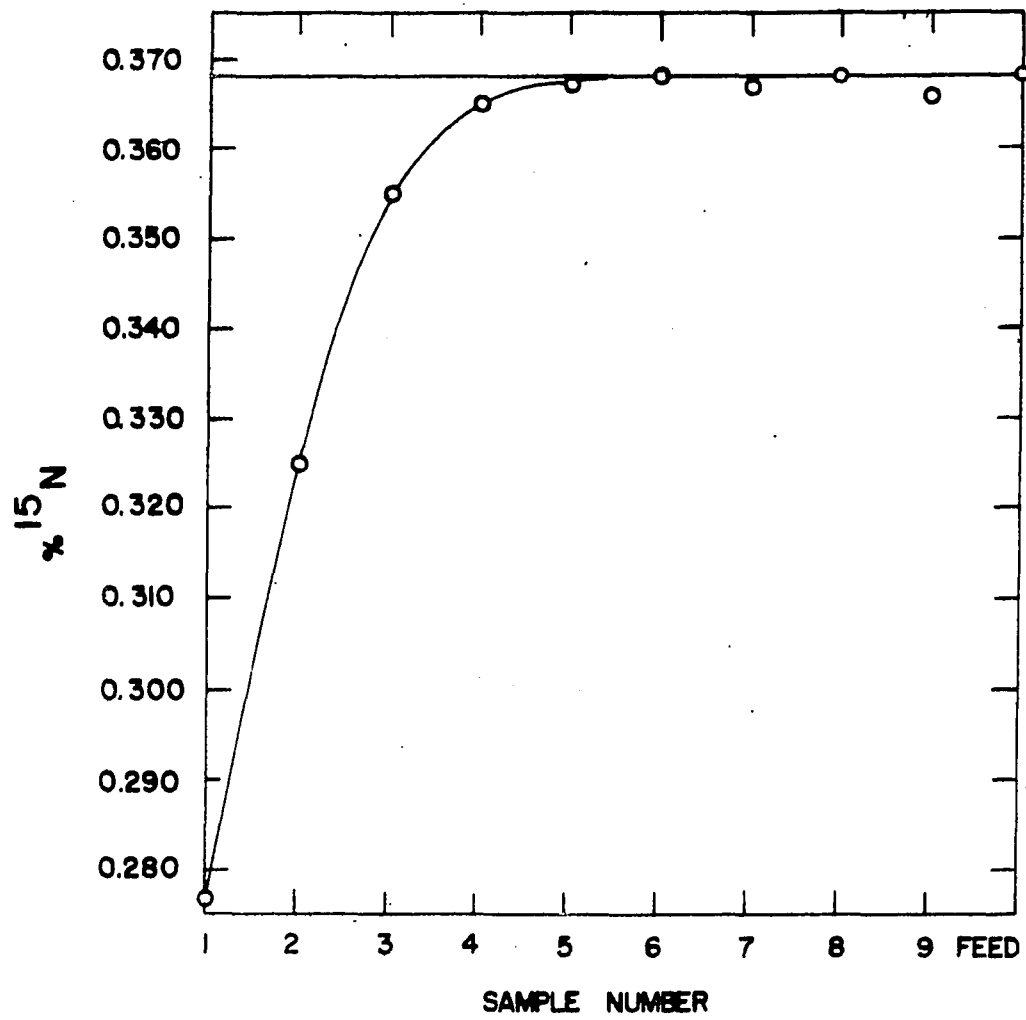


Figure 3. A plot of % ^{15}N versus sample number for the ethylamine system.

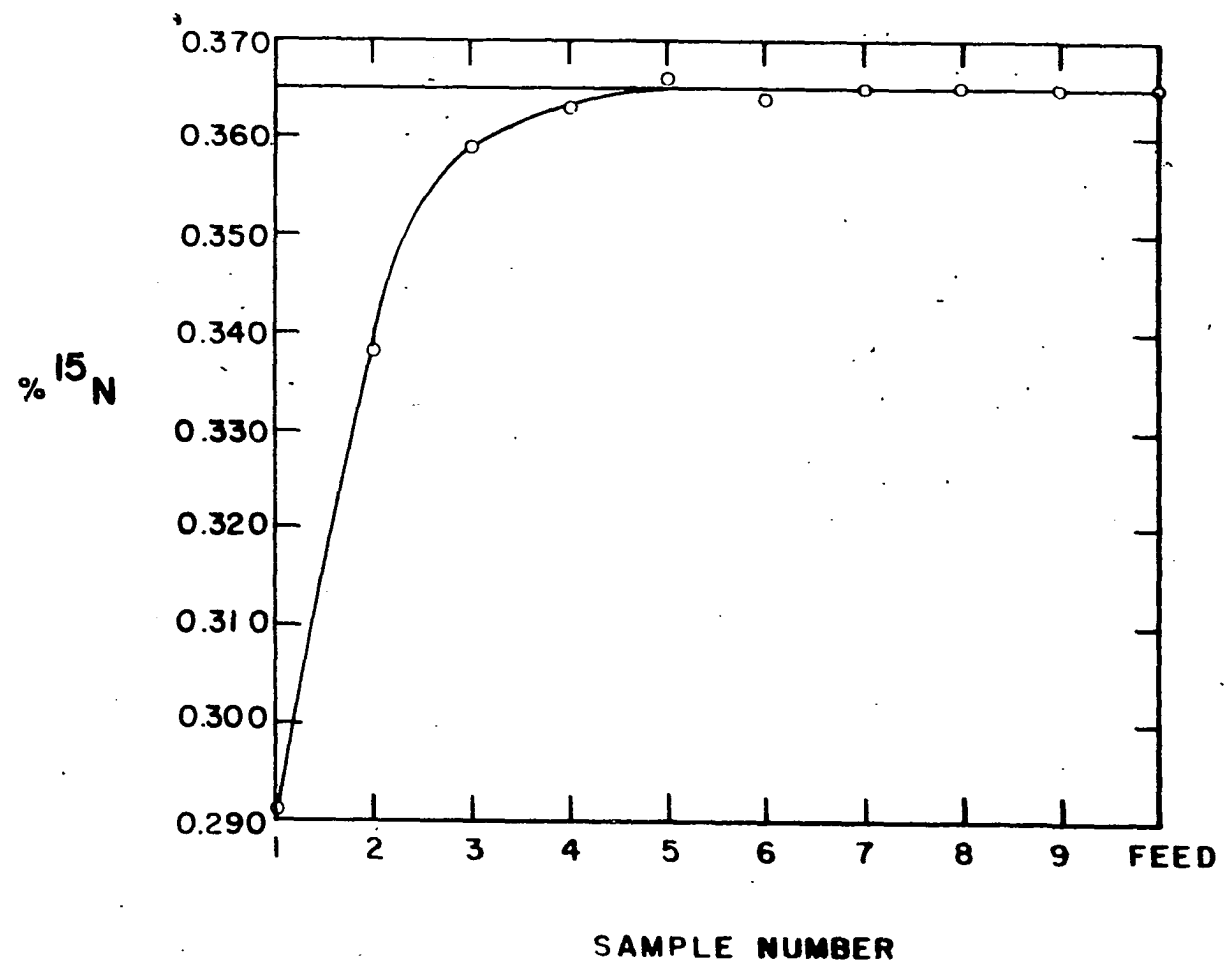


Figure 4. A plot of % ^{15}N versus sample number for the
n-propylamine system

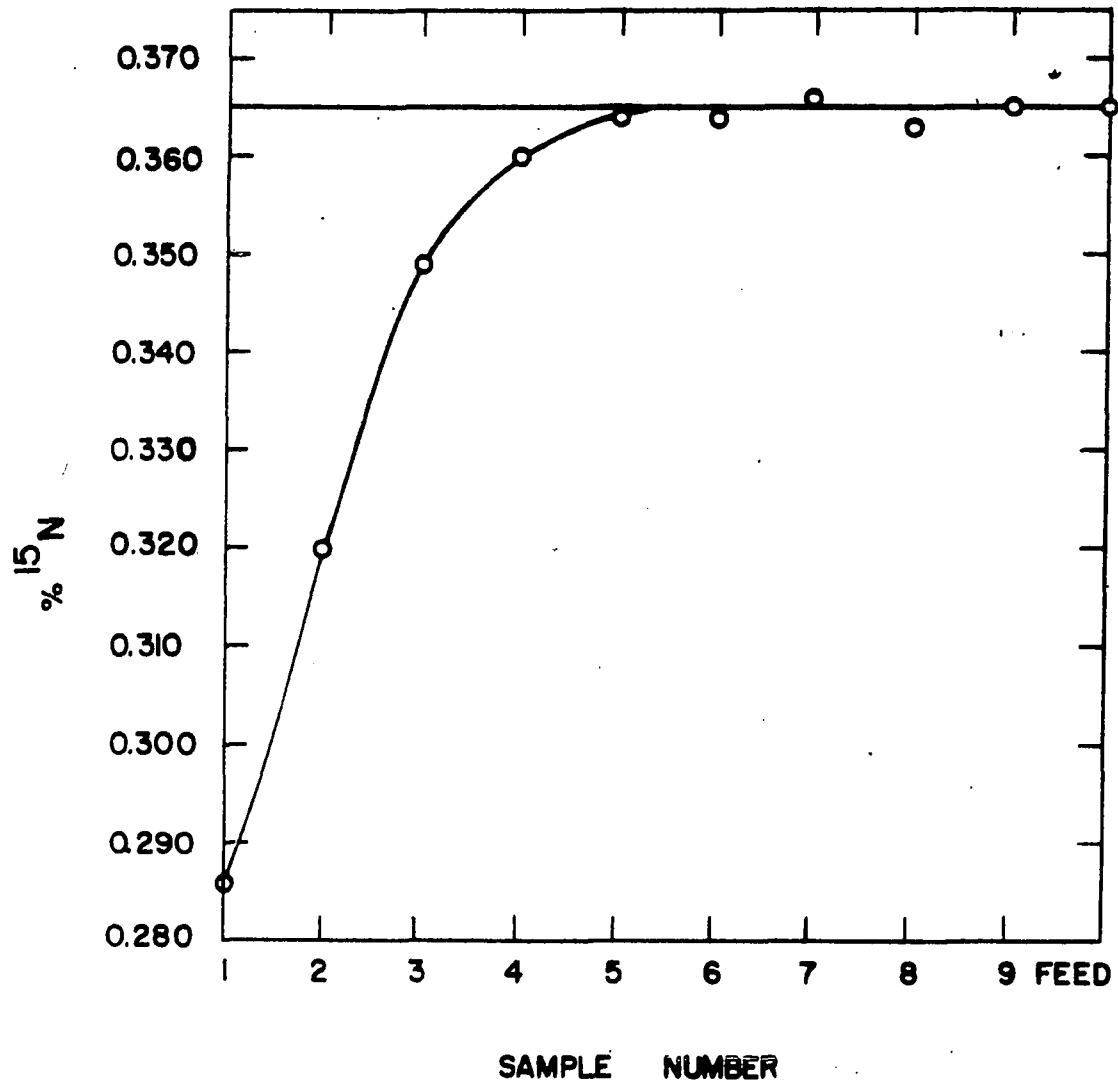


Figure 5. A plot of % ^{15}N versus sample number for the iso-propylamine system

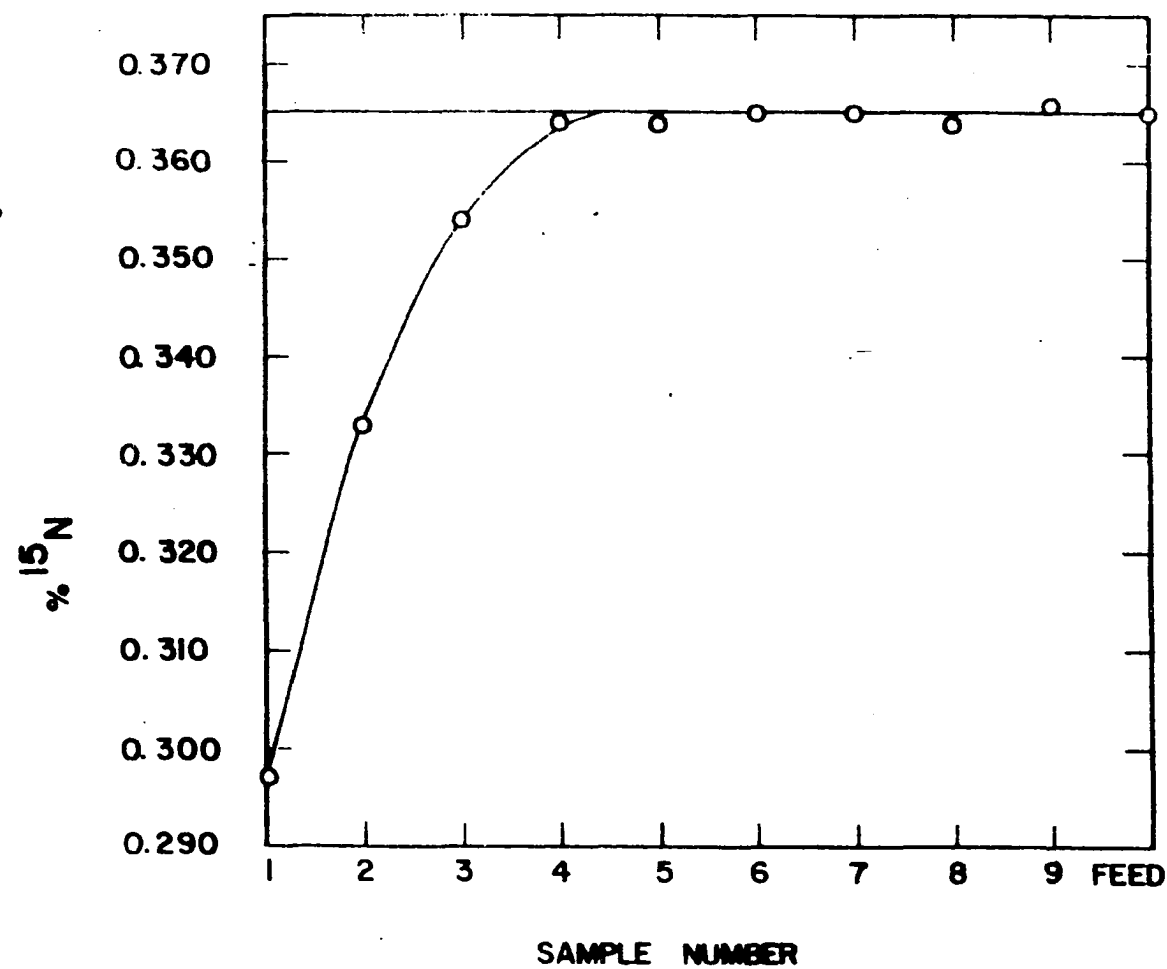


Figure 6. A plot of % ^{15}N versus sample number for the n-butylamine system

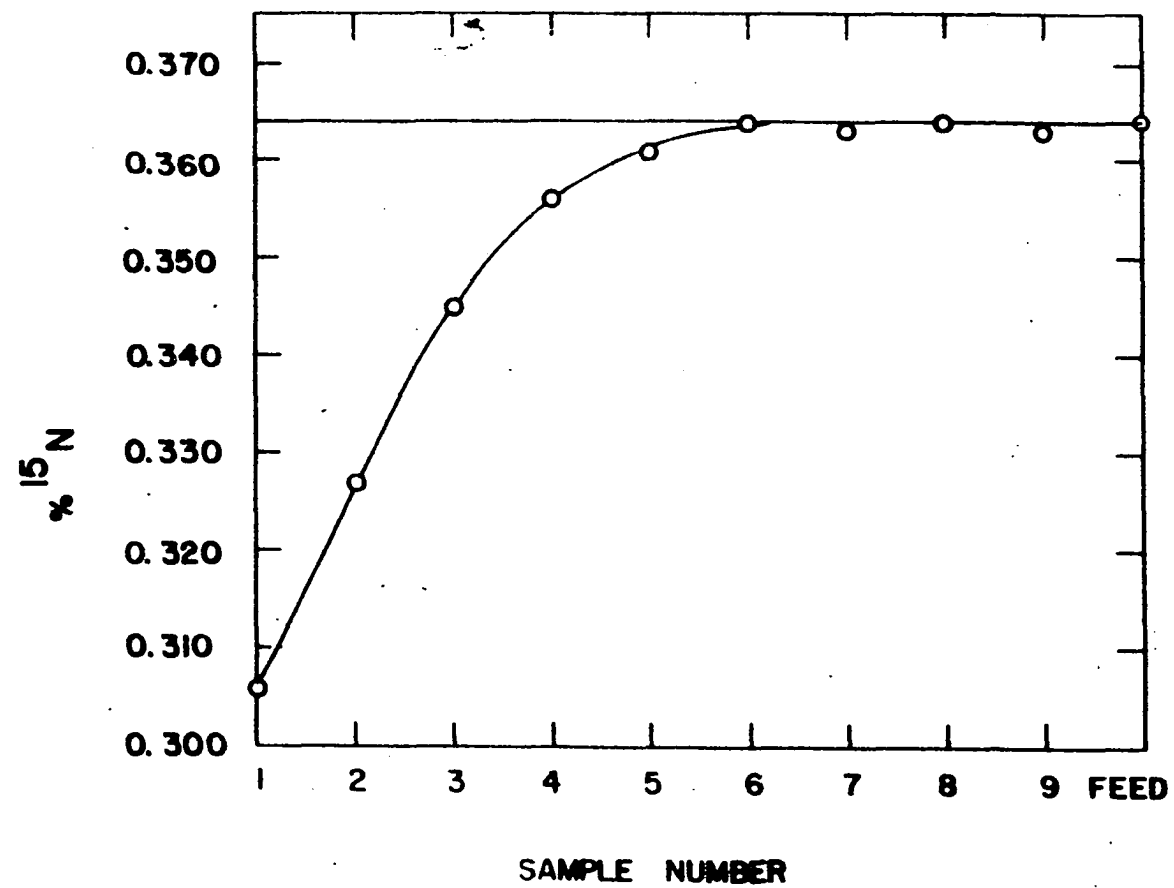


Figure 7. A plot of % ^{15}N versus sample number for the dimethylamine system

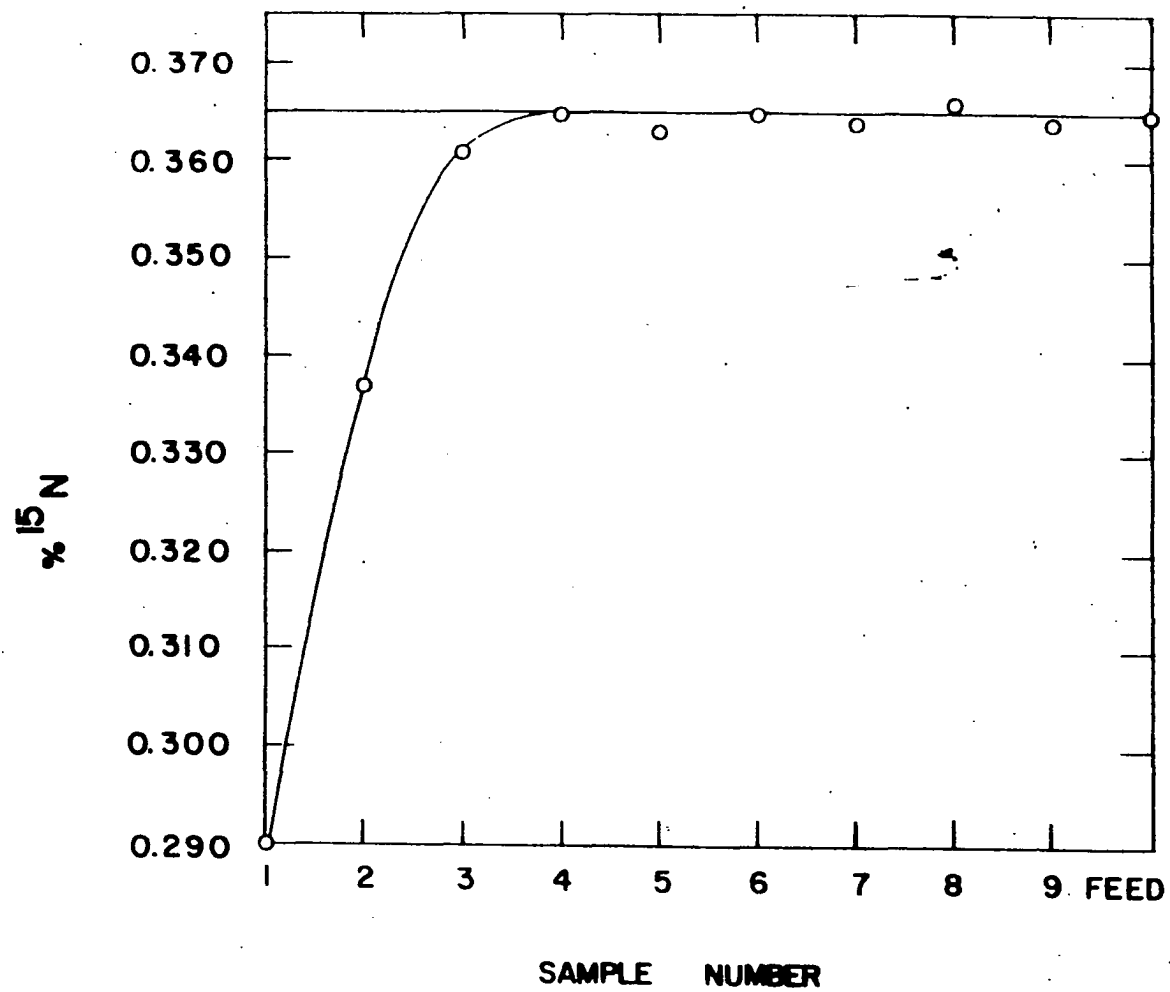


Figure 8. A plot of % ^{15}N versus sample number for the diethylamine system

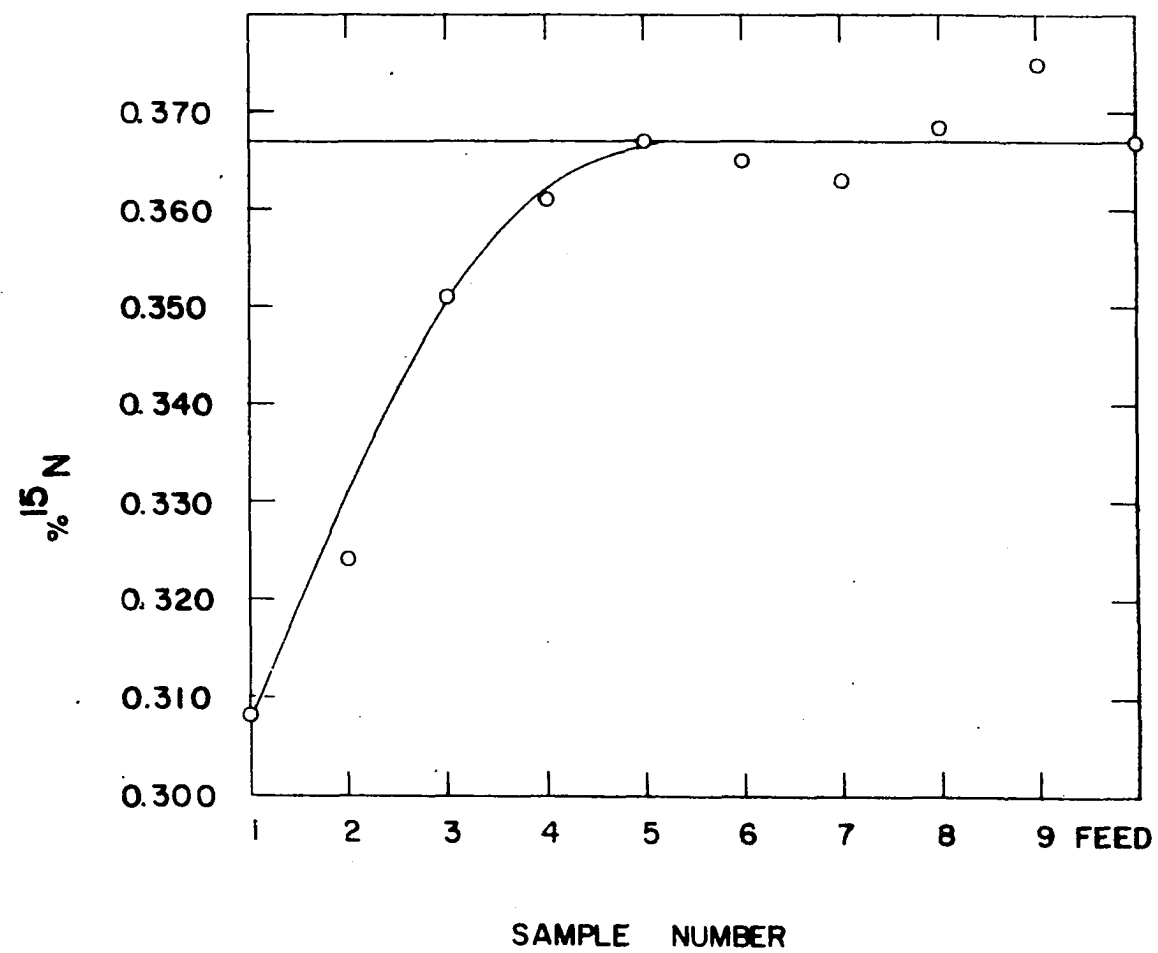


Figure 9. A plot of % ^{15}N versus sample number for the dipropylamine system

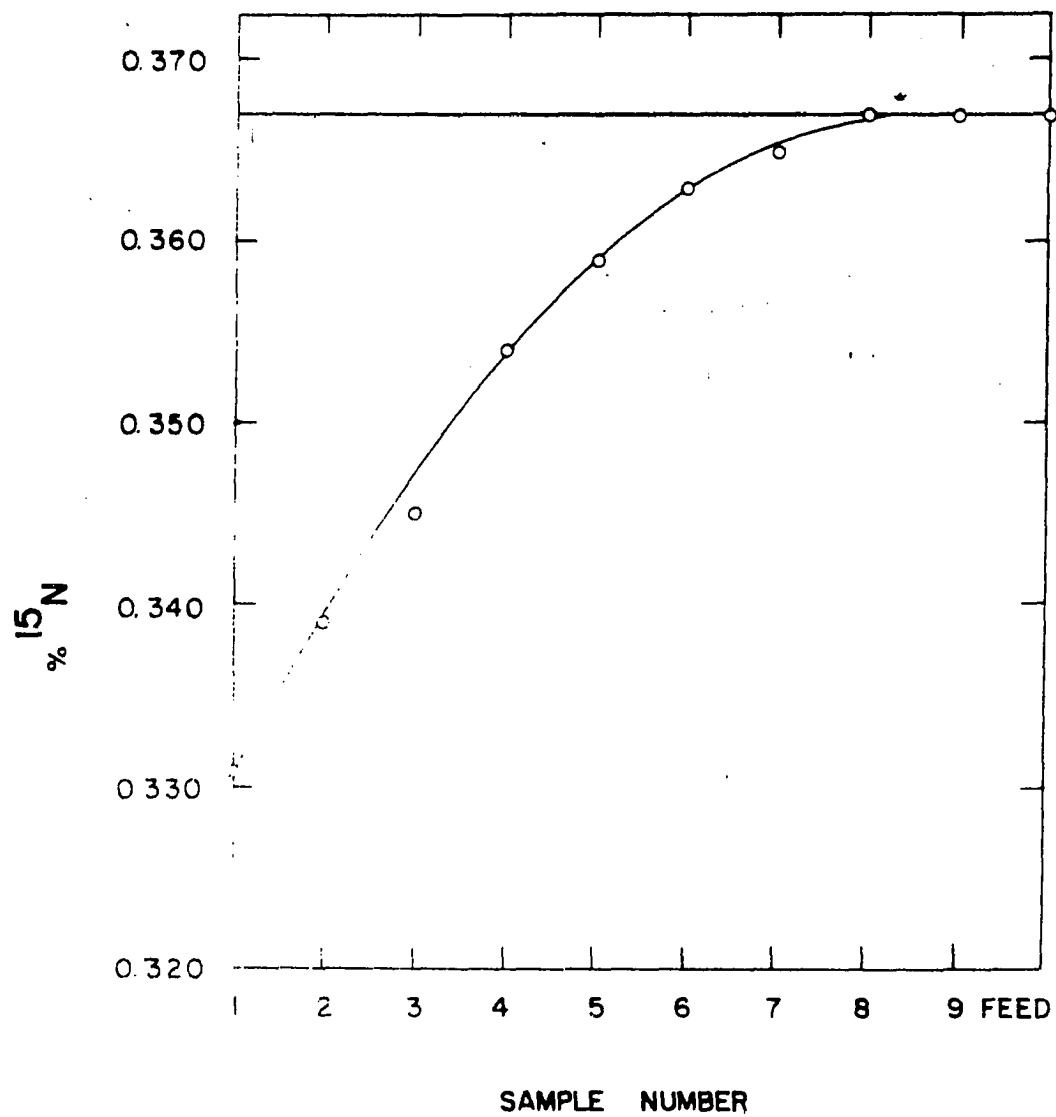


Figure 10. A plot of $\%$ ^{15}N versus sample number for the trimethylamine system

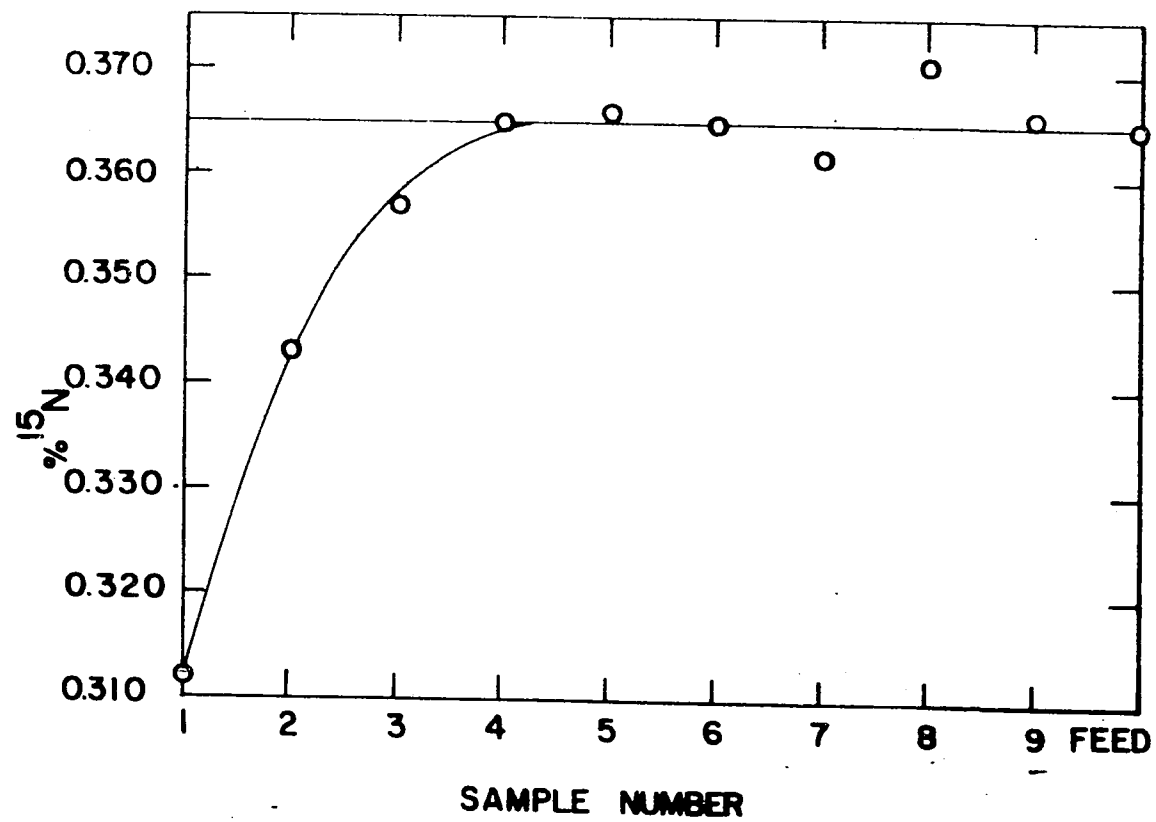
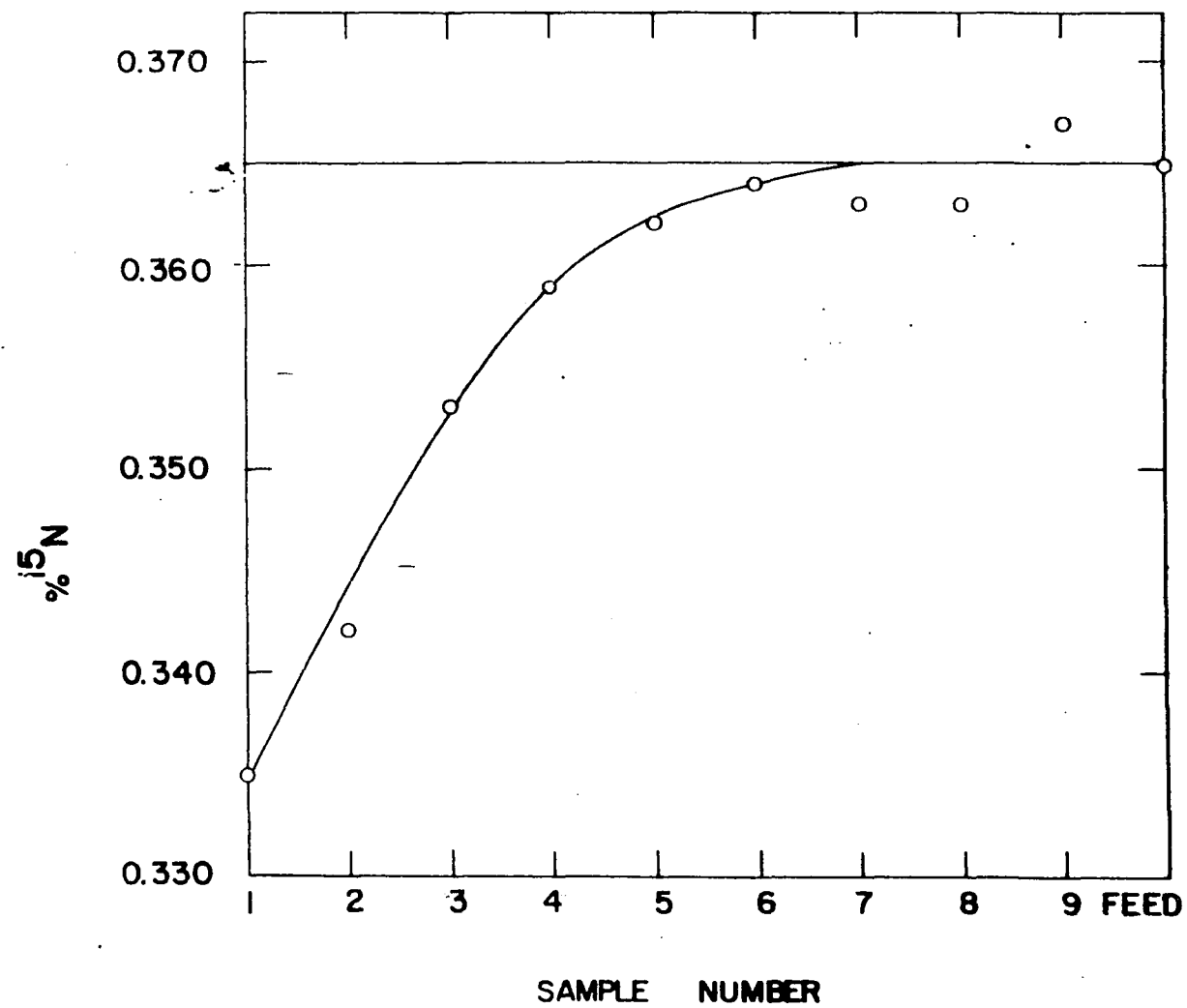


Figure 11. A plot of % ^{15}N versus sample number for the triethylamine system

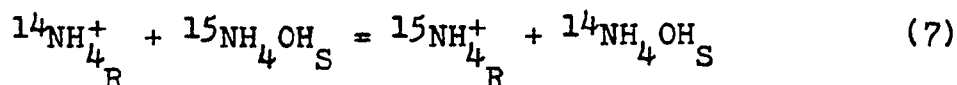


alous behavior, it appears that the theory proposed by Kakihana et al. is inadequate to explain the separation factors determined in this work.

In the following pages, a new approach will be developed that utilizes many of Kakihana's ideas and equations. This approach explains why the separation factor decreases with tertiary amines. It also explains why other workers have observed a variation in α with a change in temperature and/or concentration. It is hoped that the ideas presented here will contribute in some significant way to a better understanding of the separation factor.

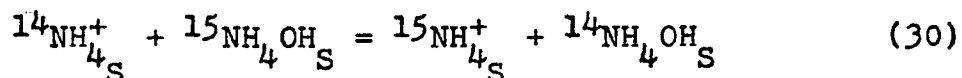
It was mentioned earlier that Equation 29 could not be used to calculate theoretical selectivity coefficients because some of the quantities in the equation could not be determined. There is a way, however, that Equation 29 can quantitatively be used to discuss the results of this work. If it is assumed that the nitrogen separation factor for the ammonium hydroxide system is known accurately, then several of the quantities on the right hand side of Equation 29 can be determined. Using the values obtained for ammonium hydroxide, it is possible to predict how these values will change for the amines in Table 2.

Powell et al. (6) measured α for the reaction

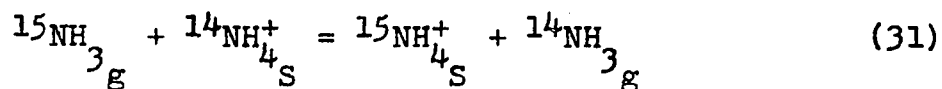


as 1.0257 ± 0.0001 . This value has been confirmed in this research and also by Comas et al. (40). This value will be substituted into Equation 29 for $\alpha_{\text{A}}^{\text{B}}$.

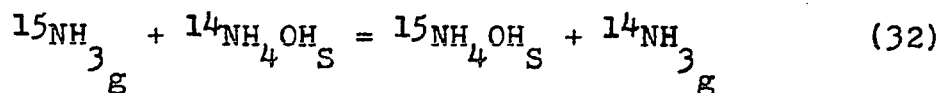
If we assume A is the lighter isotope and B the heavier isotope, then the general reaction given by Equation 25 can be rewritten for ammonium hydroxide as



The equilibrium constant, K_x , for this equation can be calculated by considering two other reactions. First, it has been found that an isotopic equilibrium exists between gaseous ammonia and an aqueous solution of an ammonium salt. The reaction is

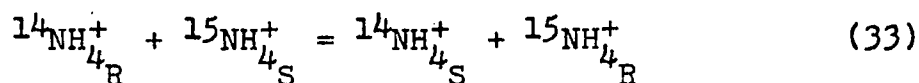


The separation factor for this reaction has been reported by Knyazev (70) as 1.034. A similar reaction using ammonium hydroxide instead of an ammonium salt can be written



The separation factor for this reaction has been determined (82, 83, 84) as 1.006. Using Equations 31 and 32, the equilibrium constant for Equation 30 can be determined. It is equal to the constant for Equation 31 divided by that for Equation 32, $K_x = 1.034/1.006 = 1.028$.

A look at Equations 30 and 7 reveals that these equations can be combined to give



This equation is similar to the general reaction in Equation 23, and $K_w = \alpha_A^B/K_x = 1.0257/1.028 = 0.9978$. It appears that this process leads to a concentration of the light isotope in the resin phase.

The original NH_4OH concentration used in this work was 0.125N. The ^{14}N in this solution was determined with the mass spectrometer as 99.635 percent. Using this information and assuming that the ionization constant for $^{14}\text{NH}_4\text{OH}$ is approximately 1.8×10^{-5} , then the last term in Equation 29 can be calculated to be $\ln 1.00034$.

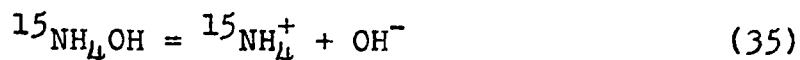
Substituting all of the above values for ammonium hydroxide into Equation 29, we can now write

$$\ln 1.0257 = \ln 1.028 + \ln 0.9978 - \ln K_y$$

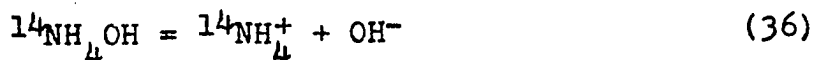
$$+ \ln \left[1 + \frac{K_y - 1}{1 + (AY)/(A_R^+)} \right] - \ln 1.00034 \quad (34)$$

It has been suggested (85) that the resin phase is equivalent to a highly ionized salt solution. If this is true, then the two unknown quantities in Equation 34 should be almost equal to one another and; therefore, cancel. Solving Equation 34 indicates that this is true.

It's obvious from Equation 34 that K_x is the largest single factor affecting the selectivity coefficient of ammonium hydroxide. It is reasonable to assume that the same is true for all of the amines studied in this work. Up to this point, K_x has been presented as the equilibrium constant for the isotopic reaction occurring between ions and molecules in the solution phase. A closer look at Equations 27 and 30 indicates that instead of K_x being the equilibrium constant for one equation, it can be visualized as the ratio of the constants for two very simple equations. Dropping the subscripts, Equation 30 could be presented as the difference between



and



We can call the equilibrium constants for these reactions the isotopic ionization constants for ammonium hydroxide. If K_{15} is the constant for Equation 35 and K_{14} is the constant for Equation 36, then $K_x = K_{15}/K_{14} = 1.028$. This leads to the conclusion that in an aqueous solution $^{15}\text{NH}_4\text{OH}$ is slightly more ionized than $^{14}\text{NH}_4\text{OH}$.

The first question that can be asked is; How can this information be applied to the separation factors determined in this work? The selectivity coefficients reported in Table 2 can be explained if we assume that as the molecular weight of the amine increases or as the amine molecule becomes more complex through additions to the nitrogen atom, the differences in the two isotopic forms of the amine are minimized. As the amines become more complex, the two isotopic ionization constants, K_{14} and K_{15} , approach one another. As the ratio of these constants decreases, the separation factor decreases. In general, anything that tends to make the two isotopic ionization constants approach one another will tend to decrease the separation factor. Anything that increases the difference in these constants will increase the separation factor. A method will be given later whereby the validity of this assumption can be

tested.

In going from primary to secondary amines, the absolute values of K_{14} and K_{15} increase, but the ratio of these two constants decreases. This results in a net decrease in the separation factor. From secondary to tertiary amines the ionization constant decreases, however, due to the increased complexity of the tertiary amines, the ratio of the isotopic constants also decreases. This results in a further decrease in the separation factor.

Now let us look at how well this new theory applies to the experimental evidence found by other researchers. It was reported earlier that several workers (26, 37, 38, 46, 47) found that the separation factor decreased with increasing temperature. Since the ionization constant of most compounds increases with temperature (86), it is reasonable to assume that both of the isotopic ionization constants will also increase with temperature. If both constants increase at the same absolute rate, then the ratio of the constants will decrease. This is what has been found experimentally.

This same type of reasoning can also be used to explain the change in the separation factor observed with changing ionic concentration. The ionization constant of most electrolytes changes significantly with concentration (87)--sometimes going through a maximum or minimum as the concen-

tration increases. Depending upon how the isotopic ionization constants vary with concentration, the separation factor can increase or decrease. Panchenkov (30) reported a very noticeable and steady decrease in the lithium separation factor as the concentration of LiOH increased from 0.005N to 5.0N. Other workers (34, 35, 48, 49), investigating other systems, have found definite maximum and minimum points in the concentration vs. separation factor curves. Most researchers have attributed this variation in α to ion pair formation.

In order to predict what would happen to the separation factor when non-aqueous solvents are used, one would have to know how the ionization constant changed in these solvents. Kakihana et al. (28, 42, 43, 48, 49) found that the selectivity coefficient varied significantly with changing solvent composition, but they did not measure the ionization constants of the solutes in these solvents.

The question now arises; How can we test the validity of the ionization constant theory? Apparently this theory does a satisfactory job of explaining much of the existing experimental data, but can it also be used to predict the separation factor of compounds not yet determined? There are a couple of experiments that could be performed to check upon this theory. For instance, the first approach

could be to prepare pure $^{14}\text{NH}_4\text{OH}$ and pure $^{15}\text{NH}_4\text{OH}$. The ionization constants of these compounds could then be measured in the same manner as the constant for natural NH_4OH was determined--the conductance method (88). This would indicate whether or not there is a difference in ionization constants between the two isotopic forms of NH_4OH . It would also tell us if this difference is the same as that predicted by the theory presented in this dissertation. If the two constants showed a measurable difference, then they could also be determined at different temperatures and concentrations. This experimental information should definitely either substantiate or deny this new theory.

Determining the nitrogen separation factor for pyridine would be another method of approaching the problem. The ionization constant for pyridine has been reported (81) as 2.3×10^{-9} . According to Kakihana's theory of ion association, this compound should have a higher separation factor than ammonium hydroxide due to the large number of molecules in the solution phase. The theory proposed in this paper predicts that the selectivity coefficient for pyridine should be much smaller than any of the amines studied thus far. Pyridine has a relatively large molecular weight and is a complex molecule. On this basis, the isotopic ionization constants for pyridine would be very

nearly the same and the ratio of the constants would be small. Unless one of the other values in Equation 34 changed significantly, the separation factor for pyridine should be small. The same procedure as used in this study could be used to determine the α for pyridine. The only modification that would have to be made is in the analytical procedure. This compound is a very weak base and probably could not be titrated accurately. Also it is quite stable toward oxidation, so a variation of the Kjeldahl method would have to be used for decomposing this amine.

In conclusion, it can be said that the nitrogen isotopic separation factor for ammonium hydroxide is significantly larger than the factor for any of the primary, secondary or tertiary amines studied in this work. If ion-exchange displacement chromatography is to be used as a means of separating nitrogen isotopes, then ammonium hydroxide will be the most efficient solute to use. Any attempt to increase the ammonium hydroxide separation factor should concentrate on maximizing the ratio of the individual isotopic ionization constants of ammonium hydroxide. Decreasing the temperature, changing the NH_4OH concentration and using non-aqueous solvents are all methods of accomplishing this result.

SUMMARY

Ion-exchange displacement chromatography was used to measure the nitrogen isotopic separation factors of ten organic amines and ammonium hydroxide. It was found that the separation factor for ammonium hydroxide was noticeably larger than for any of the amines investigated. The value of α tended to decrease slowly within any single group of amines as the length of the carbon chain increased. A more pronounced decrease in the selectivity coefficient occurred in going from one group of amines to the next, *i. e.*, from primary to secondary to tertiary amines. It is proposed that the primary factor influencing the selectivity coefficient is the ratio of the ionization constants for the two pure isotopic forms of the amines. For ammonium hydroxide, it would be the ratio of the ionization constant for pure $^{15}\text{NH}_4\text{OH}$ compared to the constant for pure $^{14}\text{NH}_4\text{OH}$. Using this ratio of ionization constants, it is possible to predict what will happen to the separation factor as the temperature, concentration or external solvent is changed.

It appears that the most profitable method of increasing the nitrogen separation factor is to concentrate on ways and means of increasing the ratio of the isotopic ionization constants for ammonium hydroxide. Decreasing the temperature, changing the ammonium hydroxide concentration

and using non-aqueous solvents are a few of the ways by which this can be achieved.

Much of the existing experimental data is explained by this isotopic ionization constant theory. However, additional work is suggested to further verify this proposal.

BIBLIOGRAPHY

1. Taylor, T. I. and Urey, H. C., J. Chem. Phys., 5, 597 (1937).
2. _____ and _____, J. Chem. Phys., 6, 429 (1938).
3. Glueckauf, E., Barker, K. H. and Kitt, G. P., Disc. Faraday Soc., 7, 199 (1949).
4. Blanco, R. E., Sessions, R. I., Kibbey, A. H. and Roberts, J. T., U. S. Atomic Energy Commission Report CF-53-6-241 Oak Ridge National Lab., Tenn. (1953).
5. Powell, J. E., Spedding, F. H. and Svec, H. J., J. Amer. Chem. Soc., 77, 1393 (1955).
6. _____, _____ and _____, J. Amer. Chem. Soc., 77, 6125 (1955).
7. Roberts, J. T., U. S. Atomic Energy Commission Report CF-52-7-132 Oak Ridge National Lab., Tenn. (1952).
8. Martin, A. J. P. and Synge, R. L. M., Biochem. J., 35, 1385 (1941).
9. Mayer, S. W. and Thompkins, E. R., J. Amer. Chem. Soc., 69, 2866 (1947).
10. Jury, S. H., U. S. Atomic Energy Commission Report CF-52-8-218 Oak Ridge National Lab., Tenn. (1952).
11. Gross, J. H., U. S. Atomic Energy Commission Report AECD-2952 Division of Technical Information Extension, AEC (1950).
12. Glueckauf, E., Trans. Faraday Soc., 51, 34 (1955).
13. Higgins, I. R. and Roberts, J. T., Chem. Eng. Prog. Symposium, Ser. No. 14, 50, 87 (1954).
14. Roberts, J. T., U. S. Atomic Energy Commission Report ORNL-2504 Oak Ridge National Lab., Tenn. (1958).
15. Higgins, I. R. and Roberts, J. T., U. S. Atomic Energy Commission Report CF-53-7-193 Oak Ridge National Lab., Tenn. (1953).

16. Higgins, I. R., U. S. Atomic Energy Commission Report ORNL-1310 Oak Ridge National Lab., Tenn. (1952).
17. Bresler, S. E. and Egorov, A. I., Khromatog., ee Teoriya i Premenen., Akad. Nauk S.S.S.R., Trudy Vsesoyuz. Soveshchaniya, Moscow 1958, 7-16 (Pub. 1960). Original not available; abstracted in Chemical Abstracts 55: 205301. 1961.
18. Dean, J. G., U. S. Patent 2,204,072. June 11, 1940.
19. Lindner, R. and Bergdahl, T., Z. Electrochem., 64, 919 (1960).
20. Blanco, R. E., Kibbey, A. H., Land, J. E. and Roberts, J. T., U. S. Atomic Energy Commission Report CF-53-11-47 Oak Ridge National Lab., Tenn. (1953).
21. Perret, L., Rozand, L. and Saito, E., U. N. Conference, Peaceful Uses of Atomic Energy, 2nd, Proc. 4, 595 (1958).
22. Studier, M. H., Brody, J. K. and Mech, J. F., U. S. Atomic Energy Commission Report ANL-5450 Argonne National Lab., Lemont, Ill. (1955).
23. Menes, F., Saito, E. and Roth, E. Separation des isotopes du lithium sur échangeurs d'ions. In "Proceedings of the Symposium on Isotope Separation," pp. 227-242, North Holland Publ. Co., Amsterdam, 1957.
24. Lee, D. A. and Begun, G. M., J. Amer. Chem. Soc., 81, 2332 (1959).
25. Powell, J. E., J. Inorg. Nucl. Chem., 24, 183 (1962).
26. Lee, D. A., J. Phys. Chem., 64, 187 (1960).
27. _____, J. Amer. Chem. Soc., 83, 1801 (1961).
28. Kakihana, H., Nomura, T. and Mori, Y., J. Atomic Energy Soc. Japan, 3, 849 (1961). Original not available; abstracted in Nuclear Science Abstracts 16: 5636. 1962.
29. Lee, D. A., J. Chem. Eng. Data, Vol. 6, No. 4, 565 (1961).
30. Panchenkov, G. M., J. Chim. Phys., 60, 107 (1963).

31. Knyazev, D. A. and Sklenskaya, E. V., Russ. J. Phys. Chem., 37, 1134 (1963).
32. Blanco, R. E. and Roberts, J. T. Separation of lithium isotopes by batch or continuous ion exchange with Decalso or Dowex-50 media. In Nicholls, C. M., ed. Technology, Engineering and Safety. Vol. 4. pp. 349-373. Pergamon Press, New York. 1961.
33. Knyazev, D. A., Russ. J. Phys. Chem., 37, 885 (1963).
34. Ciric, M. M. and Pupezin, J. D., J. Chim. Phys., 60, 100 (1963).
35. _____ and _____, Bulletin Institute Nuclear Science, "Boris Kidrich" (Belgrade), 13, No. 2, 29 (1962).
36. Yoneda, Y., Uchijima, T. and Makishima, S., J. Phys. Chem., 63, 2057 (1959).
37. Davidson, C. N., Mann, C. K. and Sheline, R. K., J. Amer. Chem. Soc., 83, 2389 (1961).
38. _____ and _____, J. Phys. Chem., 67, 1519 (1963).
39. _____, Diss. Abstracts, 23, 3644 (1963).
40. Comas, M. U., Rodriguez, T. B., Castillo, F. D. and Cellini, R. F., Anales Real Soc. Espan. Fis. Quim. (Madrid), 57B, 587 (1961). Original not available; abstracted in Chemical Abstracts 56: 12490d. 1962.
41. Spedding, F. H., J. Chim. Phys., 60, 89 (1963).
42. Kakihana, H., Nomura, T. and Kodaira, K., J. Atomic Energy Soc. Japan, 1, 419 (1959). Original not available; abstracted in Nuclear Science Abstracts 14: 8644. 1960.
43. _____, _____ and _____, J. Atomic Energy Soc. Japan, 3, 519 (1961). Original not available; abstracted in Nuclear Science Abstracts 15: 29592. 1961.
44. Holmberg, K. E., Acta Chem. Scand., 16, 1045 (1962).
45. Edinoff, M. L., J. Chem. Phys., 15, 527 (1947).

46. Harris, W. E., Betts, R. H. and Stevenson, M. D., Can. J. Chem., 34, 65 (1956).
47. Glueckauf, E., Trans. Faraday Soc., 54, 1203 (1958).
48. Kakihana, H., Ohtaki, H. and Yamasaki, K., Z. Physik. Chemie, 21, 224 (1959).
49. _____, _____, _____, Nomura, S. and Fukutomi, H., J. Atomic Energy Soc. Japan, 1, 46 (1959). Original not available; abstracted in Nuclear Science Abstracts 14: 2642. 1960.
50. Forberg, S., Barnevik, W., Gogelstrom-Fineman, I., Westermarck, T. and Ubisch, H. v. Enrichment of heavy sulphur isotopes with an anion exchanger. In "Proceedings of the Symposium on Isotope Separation," pp. 243-246, North Holland Publ. Co., Amsterdam, 1957.
51. Powell, J. E. and Spedding, F. H., U. S. Atomic Energy Commission Report IS-192 [Iowa State Univ. of Science and Technology, Ames. Institute for Atomic Research] (1960).
52. Langvad, T., Acta Chem. Scand., 8, 526 (1954).
53. Glueckauf, E., J. Amer. Chem. Soc., 81, 5262 (1959).
54. Lindner, R., Z. Naturforsch., 9a, 798 (1954).
55. Brown, W. E. and Rieman, W., J. Amer. Chem. Soc., 74, 1278 (1952).
56. Knyazev, D. A. and Mikhailichenko, A. I., Zh. Prikladnoi Khimii, 35, 66 (1962). Original not available; abstracted in Chemical Abstracts 56: 13727e. 1962.
57. Rosholt, J. N., Shields, W. R. and Garner, E. L., Science, 139, 224 (1963).
58. Kakihana, H., Gonda, K., Sato, H. and Mori, Y., Nippon Genshiryoku Gakkaishi, 5, 990 (1963). Original not available; abstracted in Nuclear Science Abstracts 18: 12528. 1964.
59. Urey, H. C. and Greiff, L. J., J. Amer. Chem. Soc., 57, 321 (1935).

60. Ogawa, E., Bulletin Chem. Soc. Japan, 2, 425 (1936).
61. Urey, H. C., J. Chem. Soc., 562 (1947).
62. Bigeleisen, J. and Mayer, M. G., J. Chem. Phys., 15, 261 (1947).
63. Rozen, A. M. and Mikhailichenko, A. I., Dokl. Akad. Nauk S.S.S.R. 148, 1354 (1963). Original not available; abstracted in Chemical Abstracts 59: 2337h. 1963.
64. Kakihana, H., J. Chim. Phys., 60, 81 (1963).
65. _____, Nomura, T. and Mori, Y., J. Inorg. Nucl. Chem., 24, 1145 (1962).
66. _____, _____ and _____, Bulletin Tokyo Institute Tech., 49, 142 (1962).
67. _____ and Kurisu, K., Nippon Genshiryoku Gakkaishi, 5, 292 (1963). Original not available; abstracted in Nuclear Science Abstracts 17: 23839. 1963.
68. Glueckauf, E. and Kitt, G. P. Gas chromatographic separation of hydrogen isotopes. In "Proceedings of the Symposium on Isotope Separation," pp. 210-226, North Holland Publ. Co., Amsterdam, 1957.
69. Bresler, S. E., Zhur. Fiz. Khim., 32, 628 (1958). Original available but not translated; abstracted in Chemical Abstracts 52: 14282c. 1956.
70. Knyazev, D. A., Russ. J. Phys. Chem., 35, 298 (1961).
71. Davies, C. W. and Owen, B. D. R., J. Chem. Soc., 1676 (1956).
72. Freeman, D. H., J. Phys. Chem., 64, 1048 (1960).
73. Chemla, M., J. Chromatog., 1, 2 (1958).
74. Glueckauf, E., J. Chim. Phys., 60, 73 (1963).
75. Powell, J. E. and Hiller, M. A., J. Chem. Education, 34, 330 (1957).
76. Betts, R. H. and MacKenzie, A. N., Can. J. Chem., 30, 146 (1952).

77. Consolidated Engineering Corporation. Operation and maintenance manual; Consolidated-Nier isotope ratio mass spectrometer Model 21-201. Pasadena, California, Author. September, 1948.
78. Diehl, H. and Smith, G. F. Quantitative Analysis. John Wiley and Sons, Inc., New York. 1952.
79. Glascock, R. F. Isotopic Analysis for Biochemists. Academic Press Inc., New York. 1954.
80. Clusius, K. and Rechnitz, G., Helv. Chim. Acta, 36, 59 (1953).
81. Hodgman, C. D., ed. Handbook of Chemistry and Physics. 35th ed. Chemical Rubber Publishing Co., Cleveland. 1953.
82. Urey, H. C. and Aten, A. H. W., Phys. Rev., 50, 575 (1936).
83. _____, Huffman, J. R., Thode, H. G. and Fox, M., J. Chem. Phys., 5, 856 (1937).
84. Thode, H. G., Graham, R. L. and Ziegler, J. A., Can. J. Res., 23B, 40 (1945).
85. Bauman, W. C. and Eichhorn, J., J. Am. Chem. Soc., 69, 2830 (1947).
86. Lewis, G. N. and Randall, M. Thermodynamics. 2nd ed. McGraw-Hill Book Company, Inc., New York. 1961.
87. Klotz, I. M. Chemical Thermodynamics. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1950.
88. MacInnes, D. A. and Shedlovsky, T., J. Am. Chem. Soc., 54, 1429 (1932).

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